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THE USE OF IMMOBILIZED BIOMASS TO RECOVER URANIUM FROM ELLIOTT LAKE TYPE ORES

FINAL REPORT

by

MARIOS TSEZOS

CHEMICAL ENGINEERING

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HAMILTON, ONTARIO

CANADA

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Contract File: DSS-38ST.23440-6-9164

Scientific Authority: Dr. R.G.L. McCready, Head CANMET Biotechnology Section.

APRIL 1988

RÉCUPÉRATION DE L'URANIUM DES MINERAIS DU TYPE ELLIOT LAKE À L'AIDE D'UNE BIOMASSE FIXÉE

RÉSUMÉ

La biomasse inactive de l'espèce microbienne Rhizopus arrhizus a été immobilisée sous forme de particules, grâce à une technique conçue à l'université de McMaster par le docteur Marios Tsezos, qui en est propriétaire. La biomasse fixée a été utilisée dans des essais en cuvée pour extraire l'uranium de solutions de lexiviats biologiques du minerai d'Elliot Lake. On a utilisé pour les essais en cuvée des solutions de procédé diluées, fournies par les mines Denison, dont la concentration initiale en uranium n'excédait pas 300 mg/L. On a d'abord ajusté le pH des solutions à 4, puis filtré le précipité obtenu. Tout d'abord, on a permis à la biomasse de se charger en uranium. On a ensuite élutrié la biomasse en cuvée avec une solution de bicarbonate de sodium à un rapport solide-liquide de 20 mg/mL. On a répété dix fois l'opération chargement-élutriation en cuvée pour observer le comportement de la biomasse. Les essais en cuvée ont montré que la biomasse fixée avait une capacité maximale d'adsorption en uranium d'environ 80 mg/g. Au dixième cycle, le chargement de la biomasse était réduit de 30%. L'uranium a été complètement récupéré après chaque cycle et les caractéristiques physiques de la biomasse se sont maintenues au cours des expériences.

On a ensuite utilisé la même biomasse fixée et les mêmes solutions de procédés dans un réacteur en continu, à lit fixe et à écoulement vers le haut dans un montage à échelle du laboratoire. On a répété 12 fois l'opération chargement-élutriation sur la biomasse fixée. Cette fois-ci, la capacité initiale de chargement en uranium de la biomasse était de 80 mg/g. Elle est ensuite passée à 50 mg/g où elle est restée stable. L'uranium adsorbé a été complètement récupéré à chaque étape, produisant des élutriats dont la concentration en uranium excédait $\overset{pas}{\vee}$5000 mg/L. La biomasse fixée est demeurée inchangée et a conservé ses caractéristiques physiques pendant les expériences.

L'utilisation de plus grands débits n'a pas changé la capacité d'adsorption de la biomasse fixée, mais elle a affecté les courbes de crevaison.

Grâce à ces résultats, il est permis de penser que la biomasse fixée a vraiment le potentiel de récupérer de façon sélective l'uranium provenant de solutions de lexiviats d'Elliot Lake.

EXECUTIVE SUMMARY

Inactive microbial biomass of the type Rhizopus arrhizus was immobilized in particulate form using the proprietary technique that has been developed by Dr. Marios Tsezos at McMaster University. The immobilized biomass was tested, in batch, for the extraction of uranium from the bioleach solutions of Elliott Lake type ore. The batch tests were carried out using dilute process solutions supplied by Denison Mines with initial uranium concentrations of up to 300 mg/L. The solutions were adjusted to pH = 4 and the resulting precipitate was filtered. The biomass was first allowed to adsorb uranium. The adsorbed uranium was then eluted, in batch, using a sodium bicarbonate solution at a solid to liquid ratio of 20 mg/mL. The batch loading-elution cycle was repeated ten times and the performance of the biomass was monitored. The batch tests showed a maximum uranium uptake capacity of about 80 mg/g for the immobilized biomass. The uptake was reduced to 30% by the tenth cycle. The uranium recovery was complete in each cycle and the biomass maintained its physical characteristics.

The same type immobilized biomass was subsequently tested using the same type uranium process solutions in an upflow continuous packed bed reactor with the help of a laboratory, bench scale pilot plant. The immobilized biomass was tested for 12 consecutive uranium uptake-elution cycles. The immobilized biomass exhibited an initial uranium uptake capacity of about 80 mg/g and a subsequent stable uranium uptake capacity of about 50 mg/g. The adsorbed uranium was fully recovered in each cycle, yielding eluates with uranium concentrations exceeding 5000 mg/L.

The immobilized biomass retained its integrity and physical characteristics throughout the experiments. The use of increased overflow rates did not affect the immobilized biomass uranium uptake capacity but affected the respective breakthrough curves.

The results have suggested that the immobilized biomass has a realistic potential for the selective recovery of uranium from the bioleach solutions of Elliott Lake.

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THE USE OF IMMOBILIZED BIOMASS TO RECOVER URANIUM FROM ELLIOTT LAKE TYPE ORES

1. INTRODUCTION

1.1 Project Scope and Objectives

The overall goal of the project was to evaluate the feasibility of the biosorption process for the separation of uranium from the bioleach solution of Elliott Lake type uranium ores in two phases. To accomplish the overall goal, the following specific objectives were established for phase I:

1) The production of immobilized biomass pellets in the 0.5 to 1 mm diameter range using the inactive biomass of Rhizopus arrhizus that has been identified previously by the author as an effective uranium biosorbent.

2) The determination of the uranium equilibrium biosorption isotherm for the R. arrhizus immobilized biomass using Denison Mines actual bioleach solutions at their natural pH and at pH = 4 to 5.

3. The determination of the instrinsic overall uranium uptake rate by the immobilized biomass, using actual Denison waste water at the natural pH and at pH = 4 to 5.

4) The determination of the uranium elution efficiency, for adsorbed uranium, using the elution conditions that have been identified earlier by the author as optimum (sodium bicarbonate solutions).

5) The determination of the number of times immobilized biomass can be used in successive uranium adsorption/elution cycles by looking at the uranium uptake capacity of the immobilized biomass and the present uranium recovery during elution in each cycle.

The first and second objectives were accomplished by growing, under the well-established conditions, the R. arrhizus biomass and by carrying out a series of batch equilibrium biosorption tests to develop biosorption isotherms using raw and immobilized biomass

with different process solutions. The kinetics of the biosorption process were examined using a batch reactor with immobilized biomass. Raw, unprocessed bioleach solution and pH adjusted bioleach solution were tested. To accomplish the fourth and fifth objectives, a series of batch loading and desorption cycles were carried out.

Rhizopus arrhizus, a fungus that has been shown to have a high uranium sorption affinity was used as the biosorbent. Except as otherwise stated, experiments were carried out using R. arrhizus biomass immobilized by our proprietary technique and actual process solutions from the Denison Mines works. Experiments were conducted with raw, unprocessed bioleach solutions, pH adjusted bioleach solutions, and pH adjusted, uranium spiked, bioleach solutions.

Phase II of the present contract focuses on the study of the behaviour of the immobilized biomass in successive biosorption-elution cycles in a laboratory scale continuous packed bed column reactor. The following detailed objectives were set for the second phase of the project:

1. Construct a bench scale continuous pilot plant that will operate during the uranium loading part of the cycle (beginning of the cycle) with pH = 4 settled bioleach solution, in a packed bed upflow mode at a fixed flow rate charged with the same type of immobilized biomass that we are presently studying and have batch data for. The size of the upflow reactor will be about 2 cm ID and 12 cm height. The pilot plant will also have provisions to wash the immobilized biomass at the end of the loading cycle with a fixed volume of water. Then the reactor will be switched to the uranium elution mode by passing through a fixed volume of sodium bicarbonate eluant at a Solid to Liquid ratio of about 20:1 mg/ml. After elution, the biomass bed will be washed again with water and revert again to the beginning of a new uranium recovery cycle.
2. Using our fermentation facilities produce R. arrhizus biomass for the preparation of the immobilized biomass pellets. The biomass will be grown under optimum conditions for biosorptive use.

3. Using our technology, immobilize enough biomass to charge the pilot plant reactor described above. This will be the same type of immobilized biomass as the one used in phase I.

4. Run the reactor continuously in multiple uranium biosorption/desorption cycles until the end of March, 1988 and for a minimum of 8 cycles.

5. During each cycle the reactor effluent will be sampled and analysed for uranium as required.

6. Two additional biosorption/desorption cycles will be carried out at 3mL/min and 6mL/min flow rates in order to provide a preliminary assessment of the flow rate effects on the biomass performance. Objective 6 was the result of a brief extension of the project approved early in 1988.

The present report is the final report to the scientific authority Dr. R.G.L. McCready of CANMET for both phases of the study (contract file: 38ST.23440-6-9164) which encompasses the objectives stated above. All the objectives have been accomplished.

2. MATERIALS AND METHODS

2.1 Bioleach Solution Processing

Two 20 L carboys of Denison Mines bioleach solution were received for use in the experimental program. These were arbitrarily labelled Solution A and Solution B. Both solutions were turbid and light yellow in colour with pH <2. Solution A was somewhat darker than Solution B. Solution A was not processed but was used as received for the experimental work. For the first biosorption experiment, Solution A was mixed to keep solids in suspension. In subsequent experiments, the supernatant of Solution A was used, as the suspended solids had settled, and no attempt was made to resuspend the settled solids.

A portion of Solution B was removed from the carboy for processing. The pH of the solution was adjusted to 4.0 by dropwise addition of sodium hydroxide solution while the solution was continuously mixed. The resulting orange coloured, ferric precipitates were

allowed to settle overnight. The precipitate settled to fill approximately half the volume of the container. The clear supernatant solution was decanated by siphoning and was filtered through a 0.45 µm membrane filter. The remaining sludge was vacuum filtered through medium laboratory filter paper. The filtrate was initially turbid, however after a thin cake formed and covered the surface, the filtrate ran clear. The turbid filtrate was refiltered with the remaining sludge through the filter cake. The sludge appeared to be readily filterable and excessive blinding of the filter did not occur although a thick filter cake was formed. The filtrate from the rough filtration was polished by filtering through a 0.45 µm membrane filter. Samples of the filtrate and the sludge cake were taken for uranium analysis.

It was observed that a significant fraction of the uranium in Solution B was precipitated in the pH adjustment process. This was partly attributed to the presence of phosphates in the solution. A third solution, labelled Solution C, was obtained from Denison Mines and was processed in the same manner as Solution B. A signficant quantity of dissolved uranium remained in Solution C after the pH adjustment process. The processed Solution C was spiked by the addition of approximately 150 mg/L of depleted uranium in the form of uranyl nitrate. This solution, together with raw Solution A and processed Solution B were used in the subsequent experimental work.

2.2 Biosorbent Production

A pure strain of R. arrhizus was grown in a twin 14 L bench top fermentor in a nutrient broth under carefully controlled conditions. Sterile conditions were used to prevent contamination by other microorganisms. The R. arrhizus was separated from the nutrient solution by filtration, was washed thoroughly and autoclaved. The biomass was then freeze dried. The dried biomass was size classified and immoblized using a proprietary immobilization process to produce particles of 20-25 mesh size. Several batches of biomass were produced and tested to compare the uranium uptake between batches. The uranium

uptake of the different batches of biomass was examined before and after immobilization and was found to be consistent.

2.3 Biosorption Isotherms

Biosorption equilibrium isotherms were determined by contacting varying quantities of raw or immoblized biomass with a given volume of the different process solutions and allowing the systems to reach equilibrium. Measured quantities of biomass were placed in screw-top flasks with measured quantities of process solution. The flasks were agitated on an orbital shaker for 7 days to allow each system to reach equilibrium. The biomass was then separated from the liquid phase by filtering through a 0.45 µm membrane filter. The filtrates were collected for uranium analysis. The biomass collected on the filters was washed with distilled water to remove any residual solution and was recovered for analysis. Uranium uptake was determined both by a mass balance on the liquid phase and by direct analysis of the biomass uranium content using a delayed neutron counting technique.

2.4 Biosorption Kinetics

The rate of the biosorption process was determined by using a specially designed, temperature controlled, Carberry type reactor as depicted in Figure 2.1. A measured quantity of immoblized biomass was placed in the rotating cage which was then placed in the reactor. The reactor was filled with a measured quantity of process solution. Tests were carried out with both Solution A and spiked Solution C. Small samples were periodically withdrawn from the reactor and analyzed for uranium. In the case of Solution C, the pH of the solution was controlled at 4.0 by an automatic pH control system. The solution temperature was controlled at 24°C ± 1° by regulating the flow rate of cooling water through the reactor jacket. By examining the sorption rate at different mixing speeds, it was determined that the mass transfer in the bulk solution had no effect on the observed sorption kinetics. Therefore the

observed biosorption rates are taken to be instrinsic rates, independent of mixing intensity in the system.

2.5 Loading-Elution Cycling

A series of loading and elution cycles were carried out in a batch mode. A measured quantity of immobilized biomass was placed in a contact vessel. The first cycle began by contacting the biomass with a measured quantity of spiked Solution C to load the biomass with uranium. Mixing was accomplished with an orbital shaker. After allowing 7 days to reach equilibrium, the biomass was separated by filtration through a 0.45 μm membrane filter, and the filtrate was collected for analysis. The biomass was washed on the filter with 250 mL of distilled water, and the wash water was collected for analysis. The biomass was then returned to the contact vessel to which was added 120 mL of 0.5 N sodium bicarbonate solution to elute the sorbed uranium. After allowing three days to reach equilibrium, the biomass was again separated from the solution by filtration and again washed with distilled water. The eluant filtrate and wash solutions were collected for analysis. The loading and elution cycle was repeated in the same manner for a total of ten cycles. During the first cycle, the kinetics of the loading and elution processes were investigated. A small sample of the loading solution was removed and analyzed after four days. It was found that 96% of the seven day uptake had been attained after four days. The small change in uptake from the fourth to the seventh day suggests that little increase in uptake would occur after seven days, therefore it was decided to use a seven day period for loading. Small samples of the eluant solution in the first cycle were removed and analyzed after two days and after four days. It was found that 99% of the seven day elution had taken place after two days, so it was decided to use a three day elution cycle.

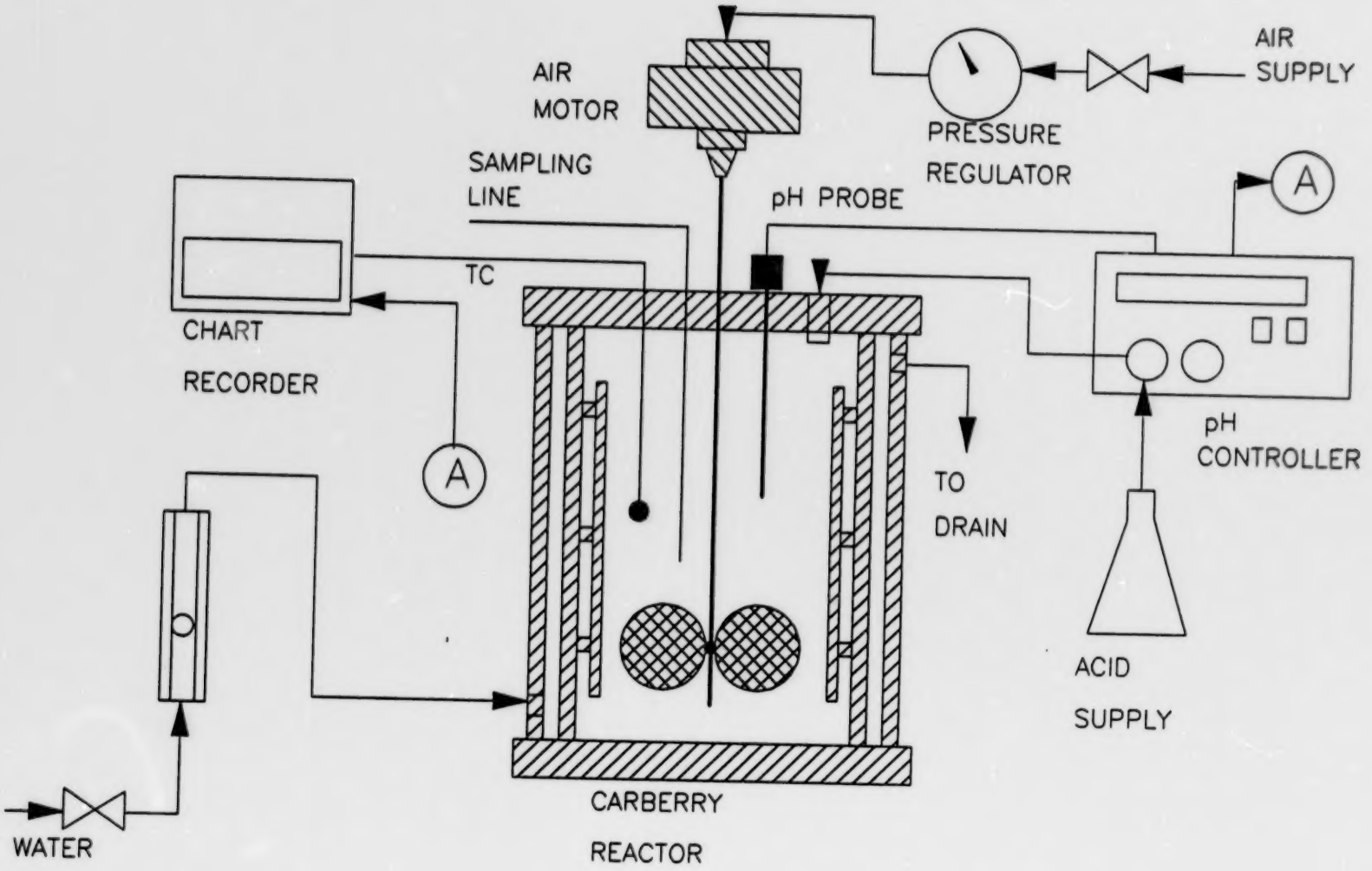

Figure 2.1 Biosorption Kinetics Experimental System

2.6 Continuous Column Experiments

A new shipment of two carboys of bioleach solution was received from Denison Mines for use in the continuous column tests which are underway. The contents of the carboys were mixed together in a stainless steel tank. Sodium hydroxide solution was added to raise the pH of the solution to 4.0. The mixing was stopped and the precipitate was allowed to settle. The supernatant solution was decanted by pumping it through a glass fibre filter into a glass collection vessel. The collected solution was used for the continuous column experiments.

The sorption column is an acrylic cylinder, 2 cm in inside diameter by approximately 15 cm in length. The column was packed with 8 g of immobilized biomass to a bed depth of approximately 10 cm. A 1 cm layer of glass beads was placed below the biomass to provide flow distribution. The column contents were retained by stainless steel screens at the top and bottom of the column. Figure 2.2 is a schematic diagram of the experimental system for the continuous column experiments.

During the loading cycle, the processed bioleach solution was pumped through the column in a upflow direction at a flow rate of 1 mL/min by a diaphragm pump. The solution leaving the column passed through a 4-way solenoid valve and into a collection vessel. Once an hour the solenoid valve was energized by a programmable controller, and the flow was diverted through a 3- way solenoid valve and then through one of two 24 port sampling valves into one of a set of sample vials. After ten minutes the solenoid valve was de-energized by the controller, and the flow was again routed to the collection vessel. A small air flow was then passed through the sample line to purge the remaining liquid to prevent contamination of subsequent samples. After ten minutes the controller momentarily energized the 24 port valve to advance the valve to the next sampling position. After one day the 3-way solenoid valve was switched by the controller to divert the sample flow to the second 24 port valve. In this way, 48 discrete samples were taken over the two day period of a loading cycle.

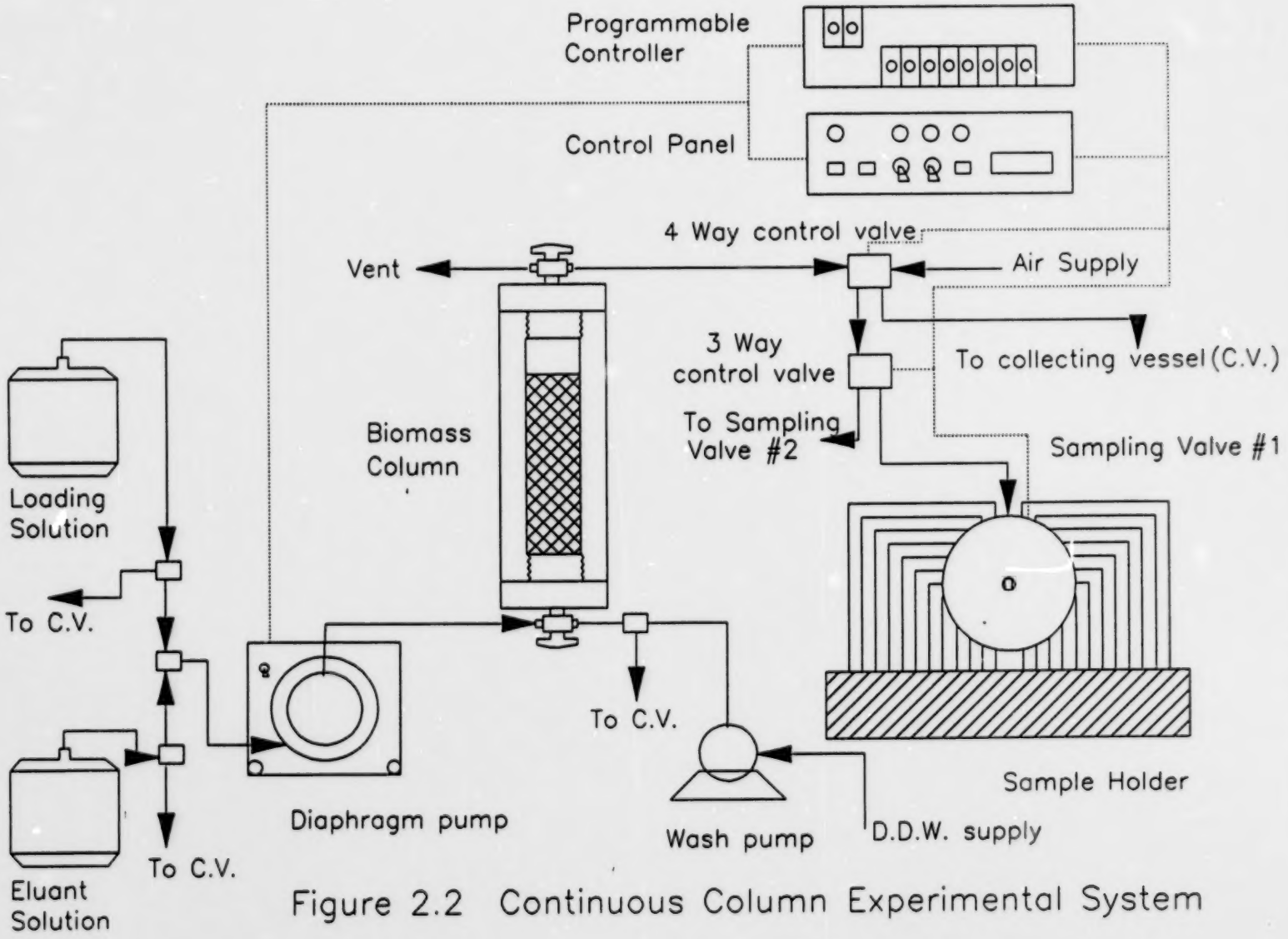

Figure 2.2 Continuous Column Experimental System

After completion of the loading cycle, the residual solution was drained from the column, and the biomass was rinsed by passing 150 mL (approximately five bed volumes) of distilled water through the bed in an upflow direction using a peristaltic pump. The feed line to the column was rinsed by reversing the diaphragm pump and pumping a portion of the rinse water in the column through the line to a waste collection vessel. The residual rinse water was then drained from the column. The residual process solution drained from the column and the rinse water solution were collected for analysis. The process solution collected over the course of the cycle was also analyzed, along with the hourly samples, to provide a measure of the total uptake of the column.

Elution was carried out by passing 840 mL of 0.5 N $NaHCO_3$ solution through the bed in the upflow direction at a rate of 1 mL/min. The elution operation was similar to the loading operation except that the duration of the cycle was only 14 hours. Hourly samples of the eluant leaving the column were collected in the same manner as the loading solution samples. After completion of the elution cycle, the column was drained of residual eluant and rinsed in the same manner as described above for the loading cycle.

Again samples of the column drain, rinse solution, and total collected eluant were analyzed along with the hourly process samples. After completion of the elution cycle, the new loading cycle was started.

2.7 Analytical Methods

Synthetic solutions containing only uranyl nitrate were analyzed for uranium using both the delayed neutron counting technique and an ICP spectrometer. All solutions containing actual bioleach process solutions were analyzed only by delayed neutron counting. The ICP spectrometric technique was not employed with these solutions because of interferences caused by contaminants in the solutions. Analyses of the spiked solution C were corrected for the different response of natural and depleted uranium. Delayed neutron

counting analysis was performed by Nuclear Activation Services Ltd. using the McMaster University nuclear reactor.

The precision of the analytical methods was checked by periodically analyzing replicate samples of different process solutions. Table 2.1 gives the results of analysis of duplicate samples by the ICP method. The mean, variance, standard deviation and coefficient of variation are given for each sample set. Replicate data for delayed neutron counting analysis are given in Table 2.2. Table 2.3 gives the mean, variance, standard deviation, and coefficient of variation for each sample set. To estimate the precision of the analytical methods, the combined, or pooled, variance, standard deviation, and coefficient of variation can be computed from the replicate data sets. The standard deviations appear to be somewhat proportional to the means, and thus the coefficients of variation are relatively constant, at least over the higher end of range of concentrations. Therefore, the combined coefficient of variation gives the most meaningful estimate of the precision of the analytical techniques. The combined coefficients of variation are given in Table 2.4 together with the 95% confidence limits for a single sample.

TABLE 2.1: REPLICATE DATA FOR ICP ANALYSIS

Uranium Concentration (mg/L)		Mean	Variance	Standard Deviation	Coefficient of Variation (%)
521.00	534.00	527.50	84.50	9.19	1.74
293.30	301.30	297.30	32.00	5.66	1.90
104.00	106.80	105.40	3.92	1.98	1.88
87.39	88.53	87.96	0.65	0.81	0.92
33.71	34.20	33.96	0.12	0.35	1.02
13.17	13.09	13.13	0.00	0.06	0.43

TABLE 2.2 REPLICATE DATA FOR DELAYED NEUTRON COUNTING ANALYSIS

Uranium Concentration (mg/L)						Mean
5250.0	4910.0					5080.0
300.0	303.4	303.1				302.2
266.4	263.9	278.3				269.5
263.0	268.0	265.0	268.0	248.0	278.0	265.0
251.2	241.6	251.7				248.2
243.8	239.9	243.3				242.1
204.0	204.0	204.0				204.0
196.0	209.0					202.5
197.5	203.8	203.4				201.6
208.0	193.0					200.5
195.4	195.4					195.4
185.0	196.0	205.0				195.3
191.3	188.3					189.8
185.7	188.6	183.2				185.8
180.7	185.0	180.4				182.0
174.3	179.7	187.0				180.3
177.0	178.0	174.0				176.3
168.6	173.2					170.9
172.0	168.0					170.0
174.1	163.8					169.0
166.5	170.7					168.6
159.8	161.6	166.4				162.6
161.0	164.0					162.5
146.0	153.0					149.5
130.9	129.9					130.4
124.0	118.0	124.0				122.0
109.2	115.6	114.7				113.2
102.7	108.7	104.3				105.2
98.8	104.0	99.5				100.8
95.5	97.3					96.4
94.9	94.4	93.2				94.2
59.2	59.7					59.5
26.5	26.3					26.4
13.1	11.7					12.4
8.9	9.9					9.4
8.6	8.5					8.6
0.1	0.1					0.1

TABLE 2.3: STATISTICS FOR DELAYED NEUTRON COUNTING ANALYSIS

Mean (mg/L)	Variance	Standard Deviation	Coefficient of Variation (%)
5080.0	57800.0	240.0	4.7
302.2	3.5	1.9	0.6
269.5	59.2	7.7	2.9
265.0	96.0	9.8	3.7
248.2	32.4	5.7	2.3
242.1	6.1	2.5	1.0
204.0	0.0	0.0	0.0
202.5	84.5	9.2	4.5
201.6	12.4	3.5	1.8
200.5	112.5	10.6	5.3
195.4	0.0	0.0	0.0
195.3	100.3	10.0	5.1
189.8	4.5	2.1	1.1
185.8	7.3	2.7	1.5
182.0	6.6	2.6	1.4
180.3	40.6	6.4	3.5
176.3	4.3	2.1	1.2
170.9	10.6	3.3	1.9
170.0	8.0	2.8	1.7
169.0	53.0	7.3	4.3
168.6	8.8	3.0	1.8
162.6	11.6	3.4	2.1
162.5	4.5	2.1	1.3
149.5	24.5	4.9	3.3
130.4	0.5	0.7	0.5
122.0	12.0	3.5	2.8
113.2	12.0	3.5	3.1
105.2	9.7	3.1	3.0
100.8	8.0	2.8	2.8
96.4	1.6	1.3	1.3
94.2	0.8	0.9	0.9
59.5	0.1	0.4	0.6
26.4	0.0	0.1	0.5
12.4	1.0	1.0	8.0
9.4	0.5	0.7	7.5
8.6	0.0	0.1	1.1
0.1	0.0	0.0	11.6

TABLE 2.4: COMBINED COEFFICIENTS OF VARIATION AND CONFIDENCE LIMITS

Method	Combined Coeff. of variation	95% confidence limit of a single sample
Delayed neutron counting	3.4%	±6.7%
ICP	1.4%	±3.7%

3. RESULTS AND DISCUSSION

3.1 Bioleach Solution Processing

Bioleach solutions were analyzed for uranium concentration and pH as received and after processing. The results of the analysis are given in Table 3.1.

TABLE 3.1: ANALYSIS OF BIOLEACH SOLUTIONS

Solution	pH	Uranium (mg/L)
A	1.8	195.4
B	1.6	189.8
B (processed)	4.0	8.6
C (processed)	4.0	159.8
C (spiked)	4.0	310.0
D	2.0	296.0
D (processed)	4.0	265.0

As noted in Table 3.1, over 95% of the original uranium content was removed from Solution B by pH adjustment and filtration. Because of this, the uranium removal process was further investigated. Three aliquots of raw Solution B were taken, and the pH of each aliquot was carefully adjusted to a different level. Each sample was filtered, and the filtrates were analyzed for uranium. The results of the test are given in Table 3.2.

TABLE 3.2: ANALYSIS OF pH ADJUSTMENT OF SOLUTION B

pH	Uranium (mg/L)
1.6	189.8
3.5	9.5
3.8	5.6
4.0	4.7

From Table 3.2 it can be seen that significant uranium removal occurs even at a pH of 3.5, and that the removal increases as the pH is increased. To confirm the uranium removal by precipitation, a sample of the precipitate from the original processing of Solution B was analyzed and found to contain 4.3 mg of uranium per gram of wet sludge.

In an additional test, a sample of solution B was adjusted to pH 2.2. and filtered. The filtrate was then adjusted to pH 3.4 and was again filtered. The results of this test are given in Table 3.3.

TABLE 3.3: RESULTS OF STEPWISE pH ADJUSTMENT OF SOLUTION B

pH	Uranium (mg/L)
1.6	189.8
2.2	110.0
3.4	26.4

This stepwise procedure was used to determine whether removal of the initial precipitate, formed at a lower pH, would eliminate the precipitation of uranium as the pH was raised. If this occurred, it would suggest that the uranium was removed by sorption onto the other precipitates. The observed results suggest that an active uranium precipitation mechanism is likely in effect, as significant uranium removal is still achieved by the stepwise pH

adjustment. The presence of phosphates in the ore leachate may have resulted in precipitation of the uranium.

When the pH of Solution C was raised to 4.0, and the solution was filtered, the filtrate was found to contain 159.8 mg/L of uranium. This solution was spiked to increase the uranium concentration by the addition of 150.2 mg/L of uranium, in the form of uranyl nitrate, to bring the uranium concentration to 310.0 mg/L. Solution C was taken from a different area of the mine than Solutions A and B, and apparently did not contain as high a concentration of the agents responsible for the uranium precipitation. Processing of Solution D by adjustment of the pH to 4.0 and separation of the precipitate only resulted in removal of approximately 10% of the original uranium concentration. The processed Solution D was used without spiking for the continuous column experiments.

3.2 Biosorption Isotherms

3.2.1 Nonimmobilized Biomass

Uranium adsorption tests were carried out to determine the intrinsic uptake capacity of different batches of R. arrhizus. The uranium uptake of non- immobilized, freeze dried biomass was assessed by contacting the biomass with a pure uranyl nitrate solution (U = 500 mg/L, pH = 3.7). Typical results of these tests are given in Table 3.4 and are shown graphically in Figure 3.1. There are minor variations in the uranium uptake capacities between the different batches of R. arrhizus. All batches are in the same general range. The observed uptake capacities are approximately the same as observed in the past with R. arrhizus biomass. For Batch 1 the isotherm is relatively flat and shows a relatively high uptake at low solution concentrations.

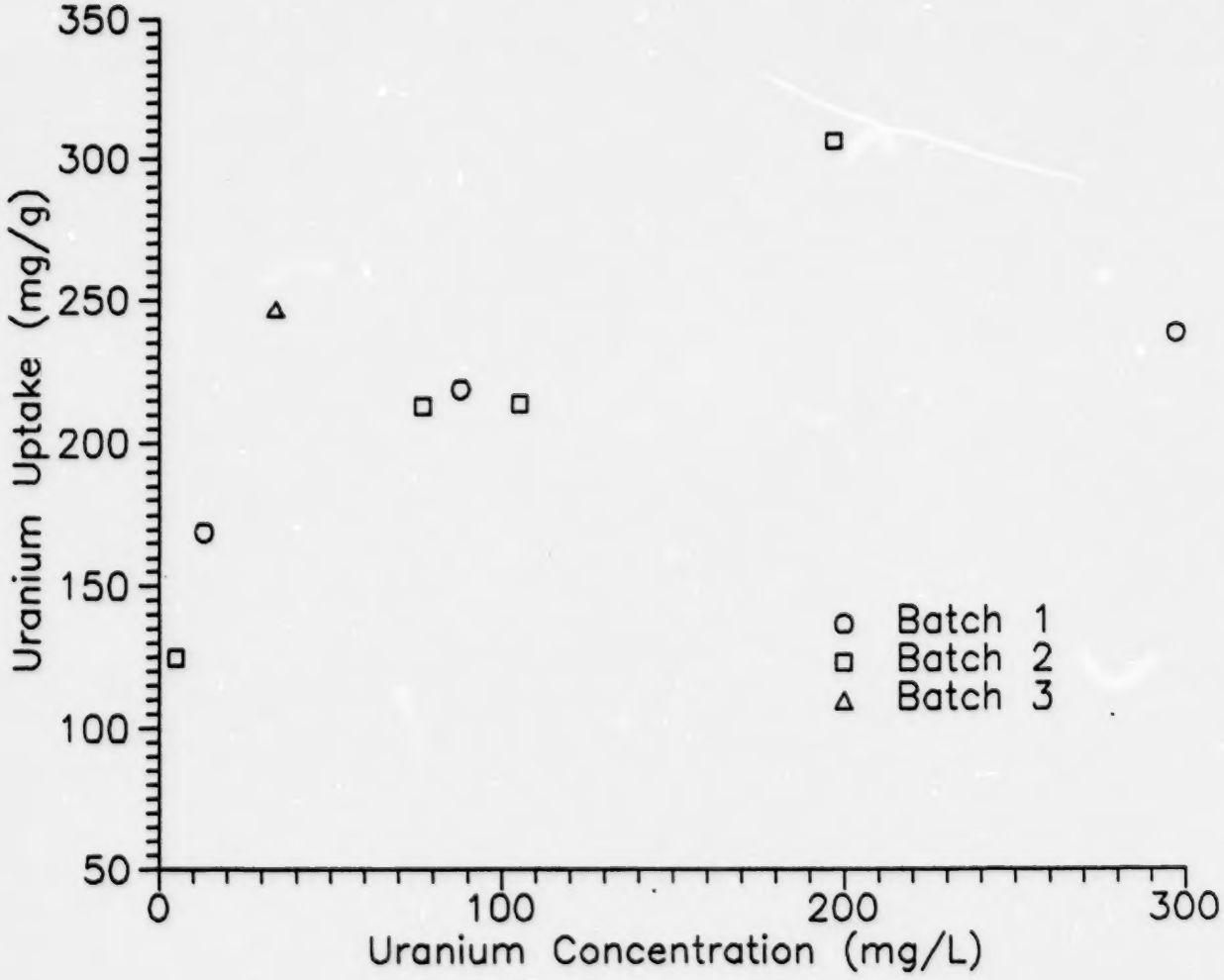

Figure 3.1 Uptake from Uranyl Nitrate Solution by Nonimmobilized Biomass

TABLE 3.4: URANIUM UPTAKE BY NONIMMOBILIZED R. arrhizus

Biomass Batch	Equilibrium Uranium Concentration (mg/L)	Uranium Uptake (mg/g)
1	297.3	239
1	88.0	219
1	13.1	169
2	197.0	307
2	105.4	214
2	77.0	213
2	4.9	125
3	34.0	247

The isotherm for Batch 2 is somewhat less flat than that of Batch 2 but still exhibits relatively high uranium uptake at low solution concentrations. The single point for Batch 3 also suggests a high uptake at low solution concentration. The high uptake at low solution concentration is a desirable property of the biomass for process applications in that the uranium from low concentration process solutions could be concentrated on the biomass and eluted at high concentration.

Adsorption tests were also carried out by contacting nonimmobilized biomass with processed Solution B. The test results are shown in Table 3.5 and graphically in Figure 3.2. Since the initial concentration of Solution B was low, the isotherm covers the low end of the concentration range. Over the observed range, the isotherm appears to fit a logarithmic relationship of the form,

$$q = 12.7 \ln C + 14.4$$

where

q = uranium uptake onto biomass, mg/g

C = uranium concentration in solution, mg/L

In this case the uranium uptake is still relatively high at a concentration of approximately 3 mg/L.

3.2.2 Immobilized Biomass

Biosorption tests were carried out by contacting immobilized biomass from Batch 3 with Solution A, processed Solution B, and processed Solution D. The results of these tests are given in Table 3.6 and are shown graphically in Figures 3.3-3.5. Tests were also carried out with immobilized biomass from Batch 1 and Solution A and spiked Solution C. The results of these tests are given in Table 3.7 and graphically in Figures 3.6 and 3.7. The uranium uptake of immobilized biomass from actual process solutions is less than the uptake of non-immobilized biomass from pure uranyl nitrate solution. The reduction of the uranium uptake capacity is probably due to the presence of many other ions in the process solutions that compete with the uranium for biosorption. The uptake from unprocessed Solution A (pH = 1.8) is much lower than from processed Solutions C and D (pH = 4.0). This is the result of the lower pH of Solution A in which the uranium tends to favour the dissolved rather than the sorbed state. In addition, Solution A probably had higher concentrations of competing and interfering materials than Solution C or D since some of these components were probably precipitated by the pH adjustment. The isotherms for Solution A are relatively flat over the range of data (Figures 3.3 and 3.6). The data plotted in Figures 3.3 and 3.6 are the data from direct analysis of the biomass since these data show less scatter than the mass balance data. Because of the low uptake from Solution A, the concentration range of the isotherms is somewhat limited. The isotherms for Solution A can be represented by linear relationships of the form,

$$q = 0.053\,C - 2.9 \quad \text{(Batch 3)}$$

$$q = 0.030\,C + 0.39 \quad \text{(Batch 1)}$$

TABLE 3.5: URANIUM UPTAKE FROM SOLUTION B BY NONIMMOBILIZED BIOMASS (BATCH 3)

Equilibrium Uranium Concentration (mg/L)	Uranium Uptake (mg/g)
2.6	26.3
0.6	9.9
0.5	3.7

TABLE 3.6: URANIUM UPTAKE BY IMMOBILIZED BIOMASS (BATCH 3)

Solution	pH	Equilibrium Uranium Concentration (mg/L)	UraniumUptake by Mass Balance (mg/g)	Uranium Uptake by Biomass Analysis (mg/g)
A	1.8	202	9.0	7.8
		202	6.1	7.6
		197	9.6	7.6
		197	6.1	7.0
		193	9.6	7.6
		192	6.2	7.3
		171	8.4	6.1
		159	5.6	5.4
B	4.0	3.20	25.5	4.5
		1.79	18.2	3.2
		0.82	10.3	1.9
		0.43	6.9	1.2
		0.36	6.9	1.2
		0.34	4.2	0.8
		0.24	2.1	0.4
		0.11	1.0	0.2

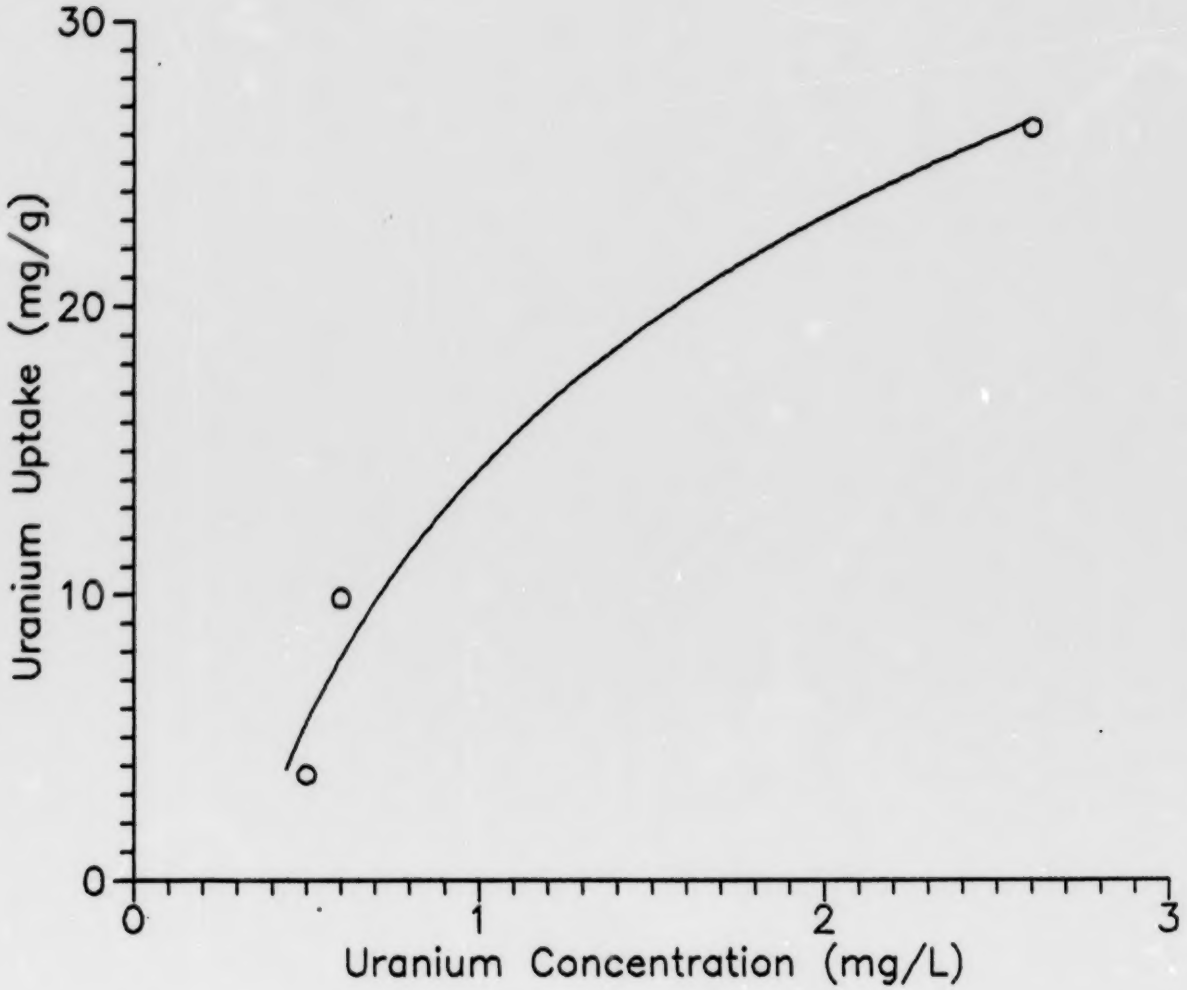

Figure 3.2 Uranium Uptake from Solution B by Nonimmobilized Biomass (Batch 3)

TABLE 3.7: URANIUM UPTAKE BY IMMOBILIZED BIOMASS (BATCH 1)

Solution	pH	Equilibrium Uranium Concentration (mg/L)	Uranium Uptake by Mass Balance (mg/g)	Uranium Uptake by Biomass Analysis (mg/g)
A	1.8	209	-	6.5
		205	-	6.7
		202	9.9	6.3
		199	12.4	6.7
		199	5.0	6.5
		198	7.4	6.3
		197	8.7	6.6
		196	4.0	5.7
C	4.0	312	24.7	79.0
		268	116.7	75.1
		267	79.0	79.1
		242	91.1	74.4
		232	103.2	75.7
		211	105.8	71.8
		179	91.3	59.8
		130	92.6	50.8

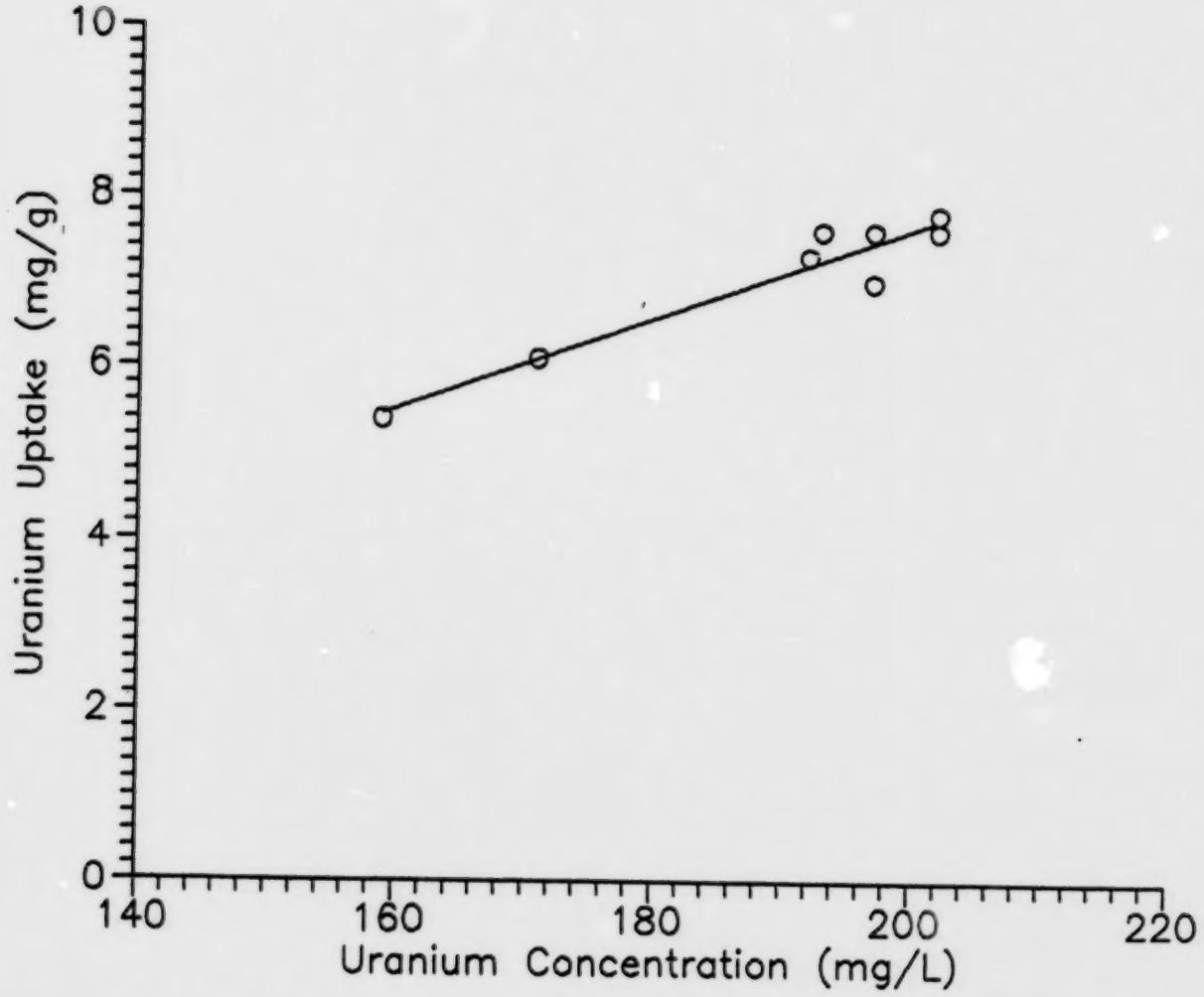

Figure 3.3 Uranium Uptake from Solution A by Immobilized Biomass (Batch 3)

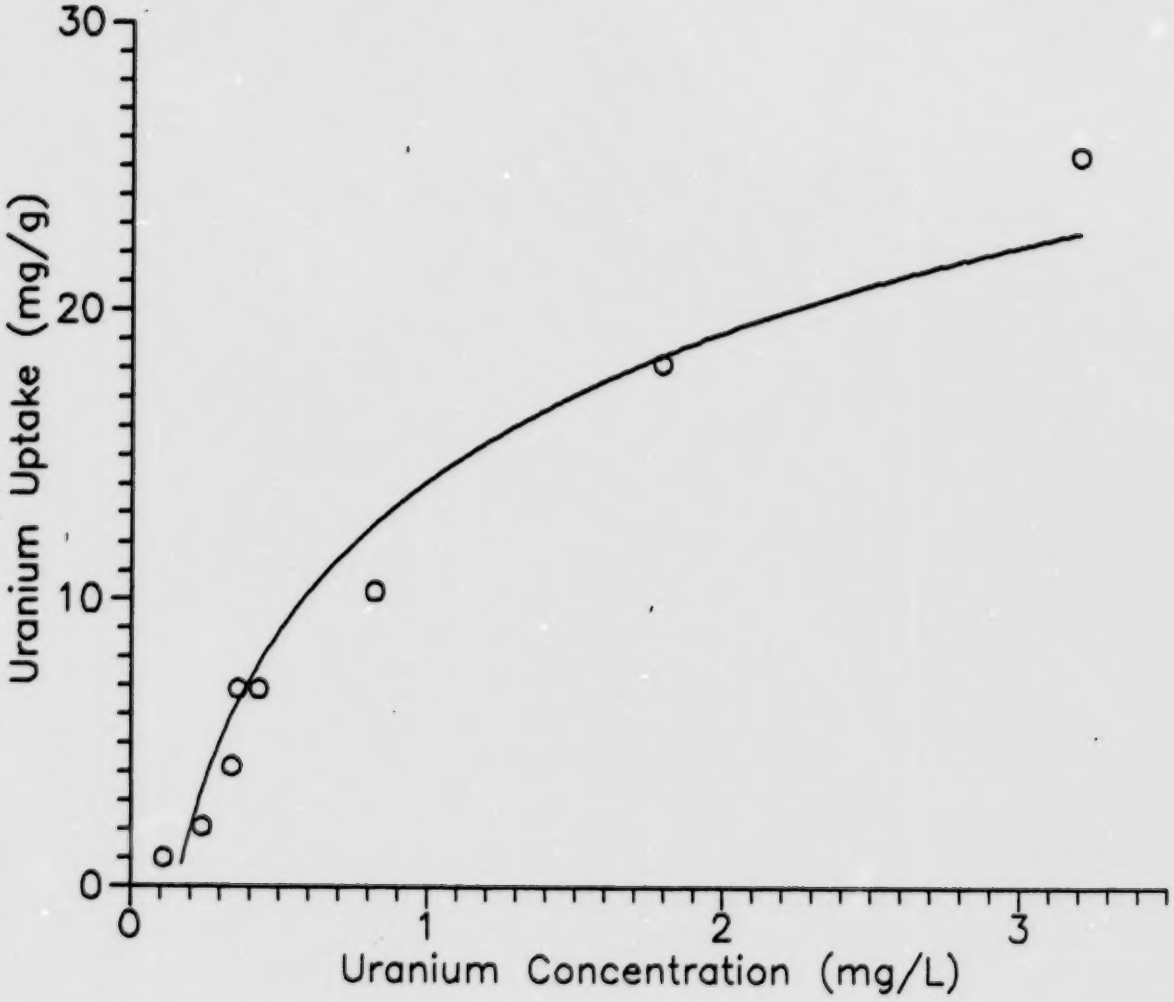

Figure 3.4 Uranium Uptake from Solution B by Immobilized Biomass (Batch 3)

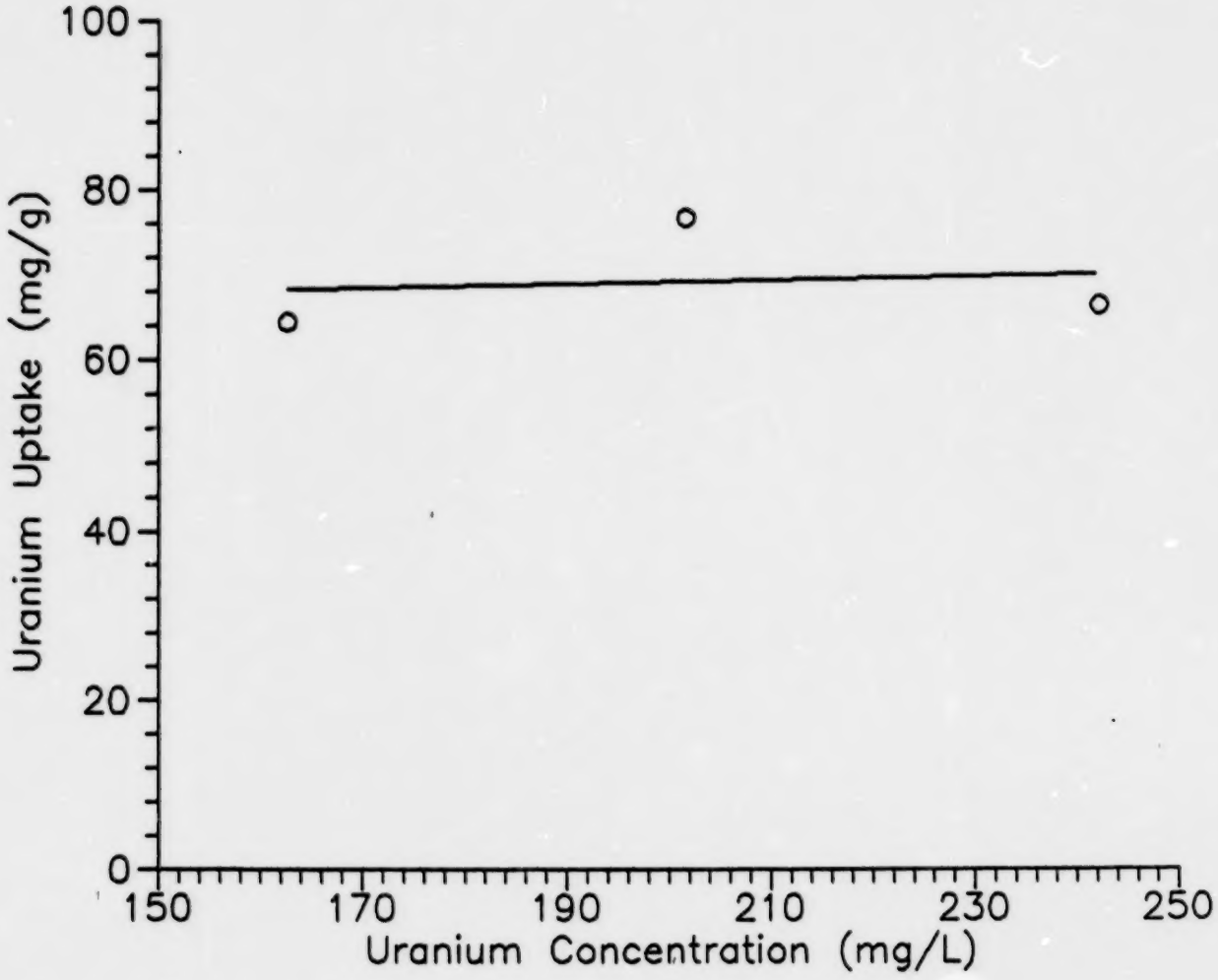

Figure 3.5 Uranium Uptake from Solution D by Immobilized Biomass (Batch 3)

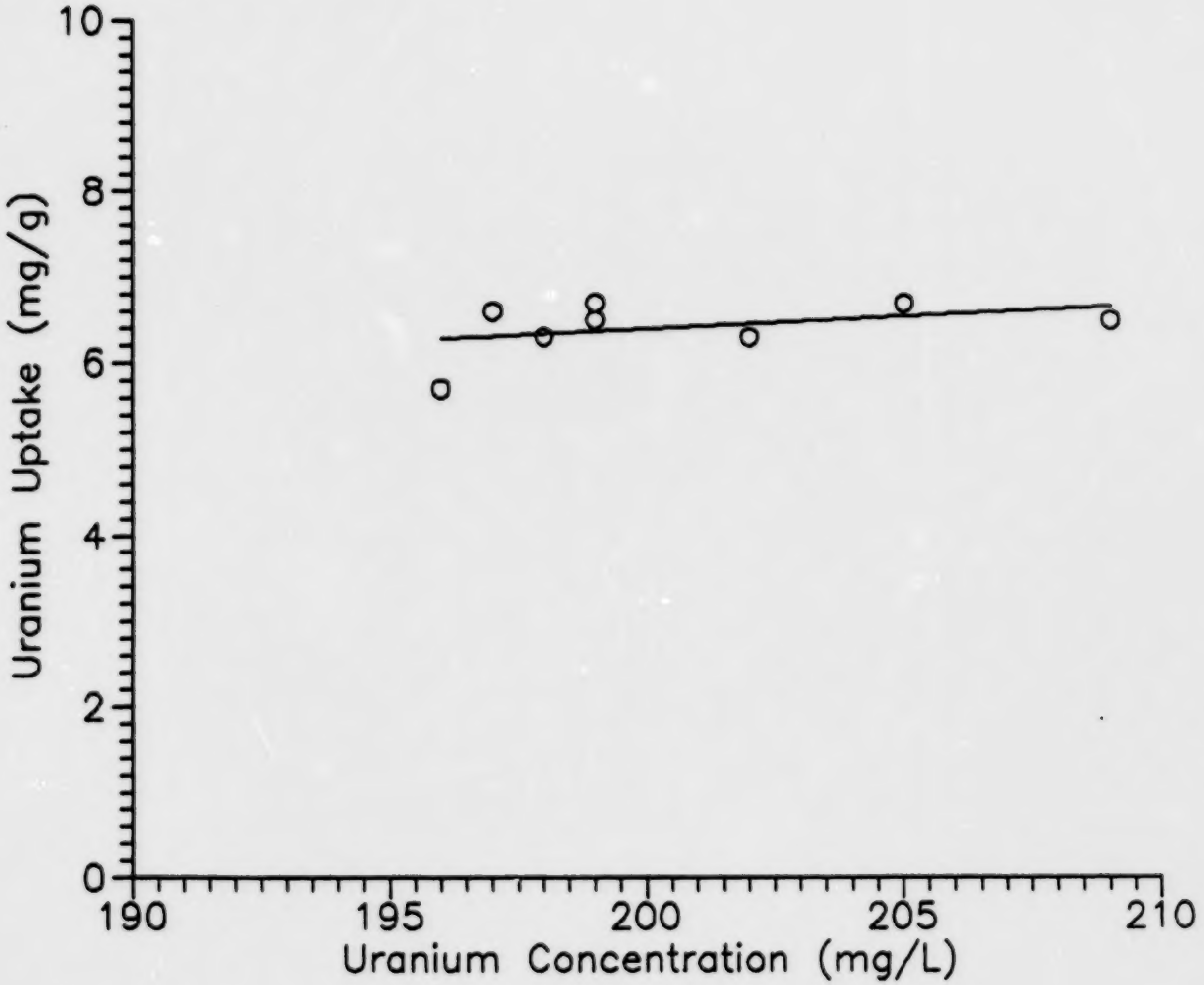

Figure 3.6 Uranium Uptake from Solution A by Immobilized Biomass (Batch 1)

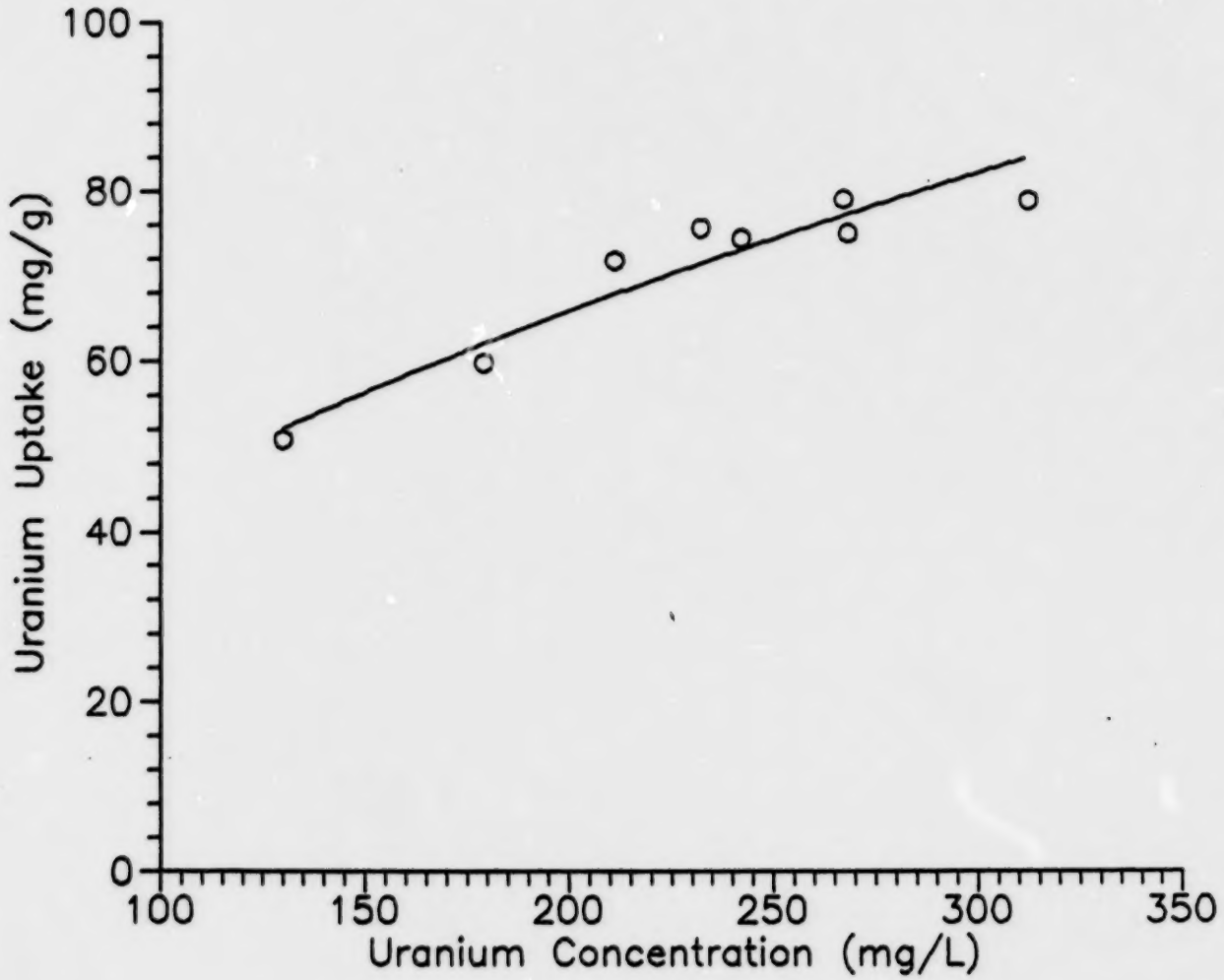

Figure 3.7 Uranium Uptake from Solution C by Immobilized Biomass (Batch 1)

Comparison of the isotherms for Solution B with immobilized and non-immobilized biomass (Figures 3.2 and 3.4) indicates that there is little difference in the intrinsic uptake between the coated and the uncoated biomass. The isotherm for the immoblized biomass (Figure 3.4) appears to fit a logarithmic curve of the form,

$$q = 7.5 \ln C + 14.1$$

The uptake from Solutions C and D are in the same range (Figures 3.5 and 3.7), although Solution C was artificially spiked with uranyl nitrate, and different batches of biomass were used in each case. The isotherm for Solution D is relatively flat over the range of concentrations covered (Figure 3.4) and can be represented by a linear relationship of the form,

$$q = 0.26\,C + 64.0$$

The isotherm for Solution C is also relatively flat over the range of concentrations covered (Figure 3.7). The data for Solution C plotted in Figure 3.7 are the data from direct analysis of the biomass as these data appeared to show less scatter than the mass balance data. However, the mass balance data appear to give somewhat higher uptake values than the direct analysis data. The isotherm for Solution C (Figure 3.7) can be represented by a Freundlich equation of the form

$$q = 3.6\,C^{0.55}$$

The sorption isotherms are all very favourable in that the uranium loading is not highly dependent on uranium concentration in solution. This is an intrinsic property of this type of biomass and is a highly desirable property for application of the biosorption process.

3.3 Biosorption Kinetics

The rates of biosorption of uranium from Solution A and spiked Solution C were determined using immobolized biomass from Batch 1. The results of the kinetics experiments with Solution A are given in Table 3.8 and are shown graphically in Figures 3.8 and 3.9. Results

TABLE 3.8: RATE OF URANIUM UPTAKE FROM SOLUTION A

Time (h)	Uranium Concentration (mg/L)	Uranium Uptake (mg/g)
0	200	0
0.017	202	–
0.033	195	2.5
0.092	203	–
0.167	198	1.0
0.250	204	–
0.500	205	–
1.00	195	2.5
2.00	204	–
4.00	184	8.0
8.00	189	5.5
20.9	191	4.5
22.5	197	1.5
29.9	188	6.0
46.5	182	9.0
69.5	193	3.5
76.1	186	7.0
94.5	184	8.0
100.6	180	10.0
118.8	185	7.5
125.5	177	11.5
197.7	188	6.0

Table 3.9: RATE OF URANIUM UPTAKE FROM SOLUTION C

Time (h)	Uranium Concentration (mg/L)	Uranium Uptake (mg/g)
0	310	0
0.072	309	0.5
0.158	294	8.0
0.256	279	15.5
0.500	268	21.0
1.00	253	28.4
2.00	222	43.9
4.00	191	59.4
6.40	178	65.9
16.3	157	76.4
25.4	144	82.8
42.7	148	80.8
46.5	138	85.8
54.3	148	80.8
67.3	144	82.8
74.3	144	82.8
91.6	138	85.8
97.8	138	85.8
114.8	139	85.3
121.8	137	86.3
139.8	138	85.8
146.3	143	83.3
186.7	139	85.3

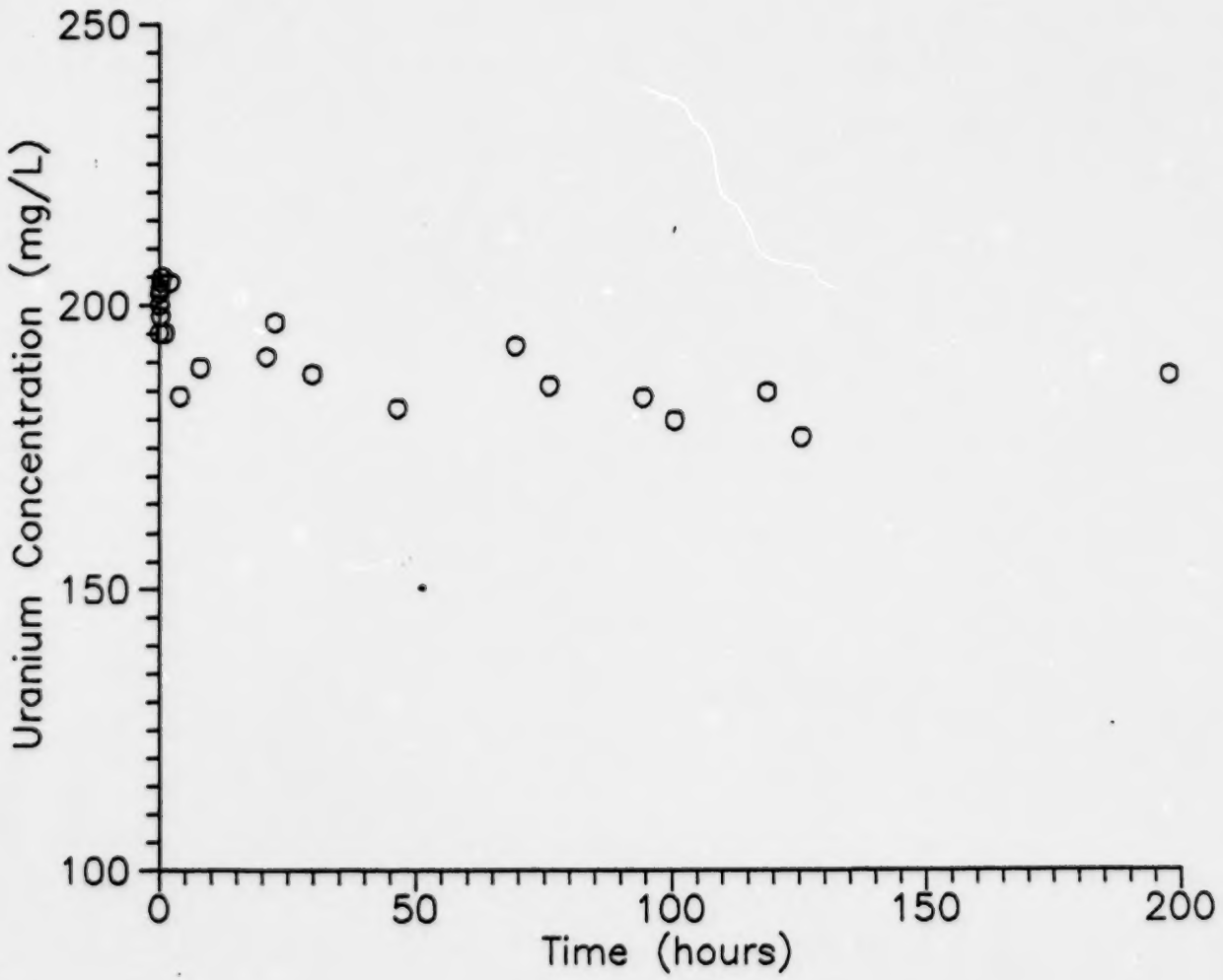

Figure 3.8 Kinetics of Uranium Uptake from Solution A

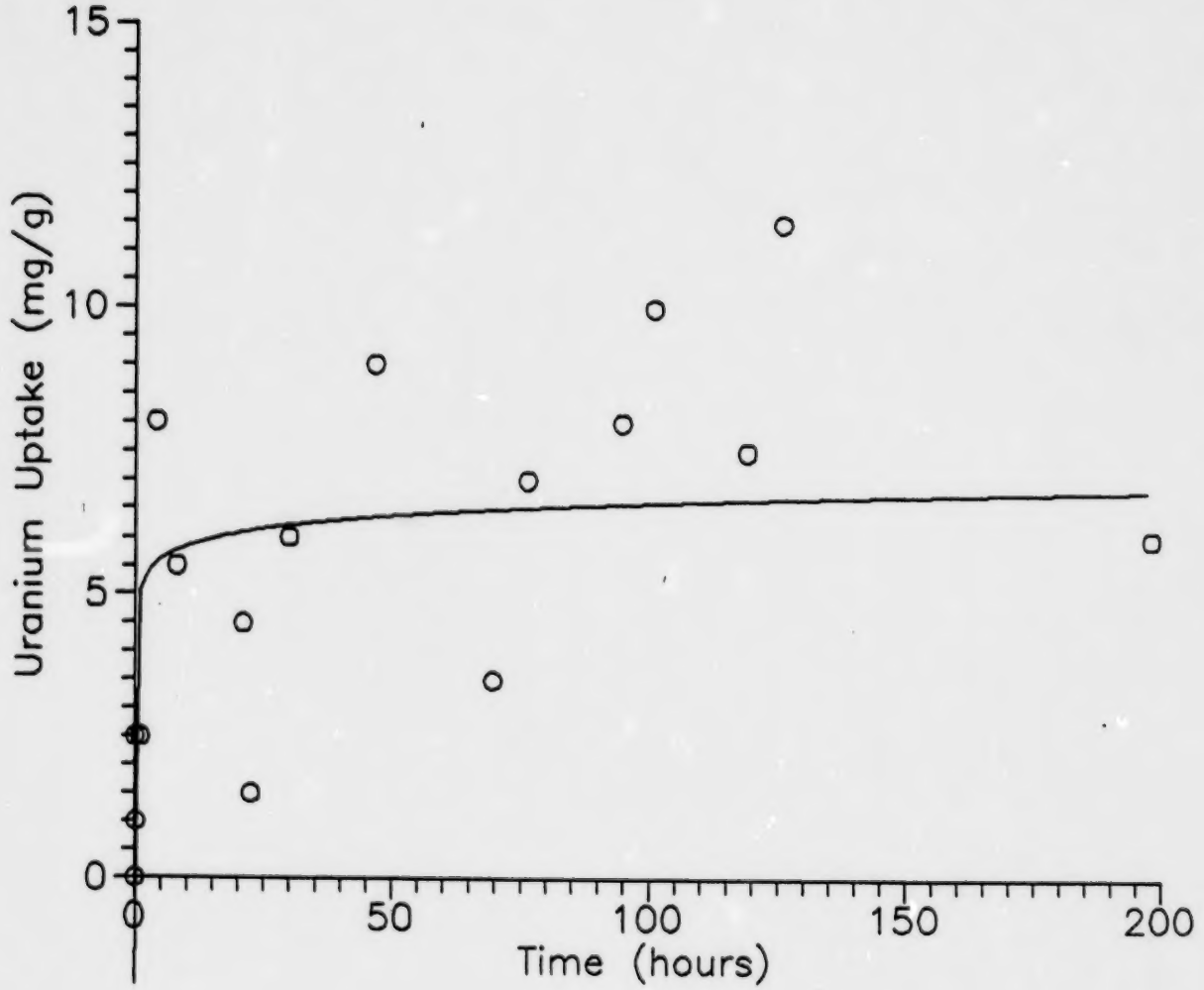

Figure 3.9 Kinetics of Uranium Uptake from Solution A

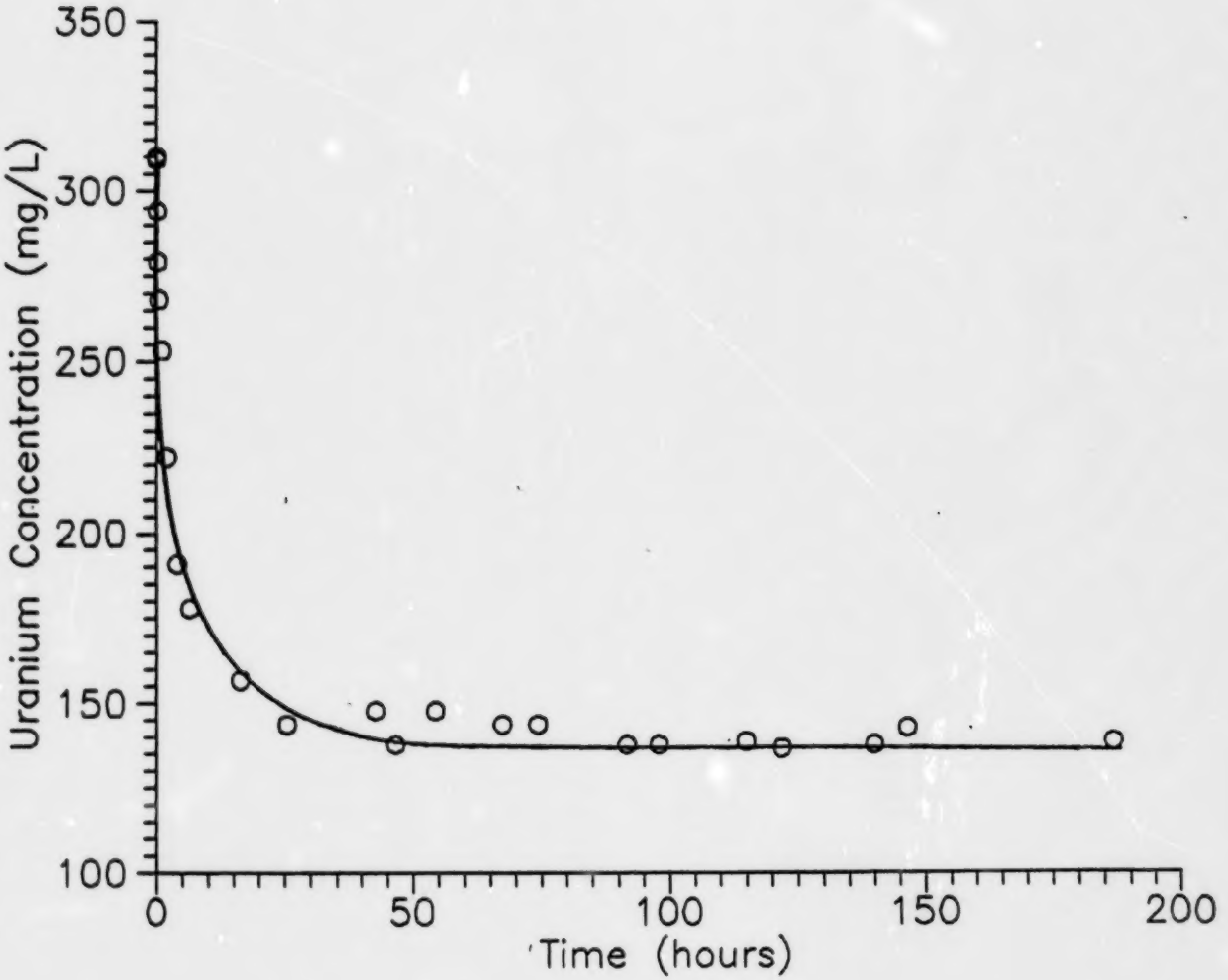

Figure 3.10 Kinetics of Uranium Uptake from Solution C

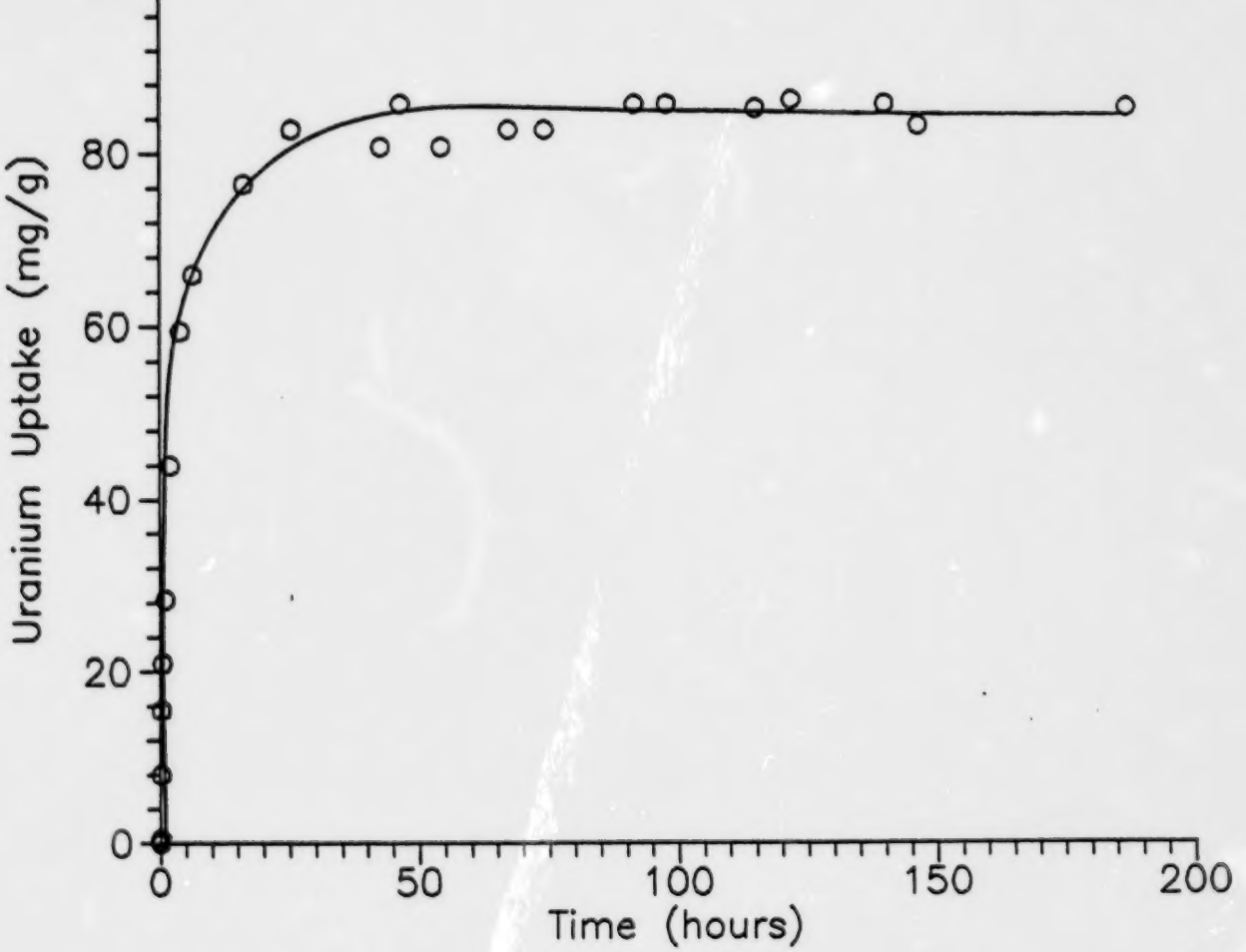

Figure 3.11 Kinetics of Uranium Uptake from Solution C

for Solution C are given in Table 3.9 and in Figures 3.10 and 3.11. For Solution A, it appeared that the system had almost reached equilibrium within a few hours. In this case, the change in solution uranium concentration was small because of the low uranium uptake capacity of the biomass.

The uranium uptake as a function of contact time (Figure 3.9) can be represented by an equation of the form,

$$q = 0.33\ \ell nt + 5.1$$

which gives a visual representation of the trend of the data. The scatter of the data is due to the small change in concentration because of the low uptake from solution A.

With Solution C, a greater concentration change was produced and 93% of the equilibrium loading is achieved in approximately 16 hours, and 80% of the equilibrium loading is reached in approximately 6 hours (Figures 3.10 and 3.11). The kinetic data for Solution C did not fit a simple functional relationship. The curves shown in Figures 3.10 and 3.11 have been hand drawn to more clearly show the trend of the data.

3.4 Loading-Elution Cycling

Ten cycles of uranium loading and elution were carried out in a batch process using immobilized biomass and spiked Solution C. The uranium uptake per gram of biomass and the quantity or uranium eluted per gram of biomass after each cycle are given in Table 3.10 and are shown graphically in Figure. 3.12. The uranium uptake in the first cycle is similar to the uptake observed in the biosorption isotherm tests. The quantity eluted in the first cycle compares well with the loading, indicating that the uranium is completely eluted from the biomass. In subsequent cycles, the uranium uptake became progressively lower after each cycle. The decrease in loading was greatest between the first and second cycles and appeared to diminish progressively after each cycle. After three cycles the uranium uptake was reduced to approximately half the initial uptake. The pH of the loading solution was checked

TABLE 3.10: LOADING ELUTION CYCLING RESULTS

Cycle	Uptake (mg/g)	Elution (mg/g)	%Eluted
1	77.2	79.3	103
2	50.0	53.5	107
3	39.9	44.0	110
4	35.9	39.0	109
5	36.5	34.0	93
6	32.5	31.8	98
7	30.3	29.5	97
8	27.3	27.5	101
9	29.3	26.3	90
10	22.1	24.6	111

after the first three cycles and found to be equal to the initial loading solution pH (4.0), in each case. This indicates that there is no pH change caused by residual eluant in the biomass, which could cause the reduced uptake. After ten cycles the immobilized biomass uranium uptake was about 30% of the initial uptake. The quantity of uranium eluted after each loading cycle corresponded well to the quantity loaded, indicating that complete elution was achieved each time. This suggests that the biosorption process is completely reversible and that the decrease in uptake capacity cannot be accounted for by an accumulation of irreversibly sorbed uranium on the biomass. After completion of the ten cycles the biomass was air dried and weighed. It was found that approximately 43% of the original biomass weight had been lost during the loading-elution cycles. Approximately 12% of the weight of the immobilized biomass is contributed by the immobilization additives. Assuming that the

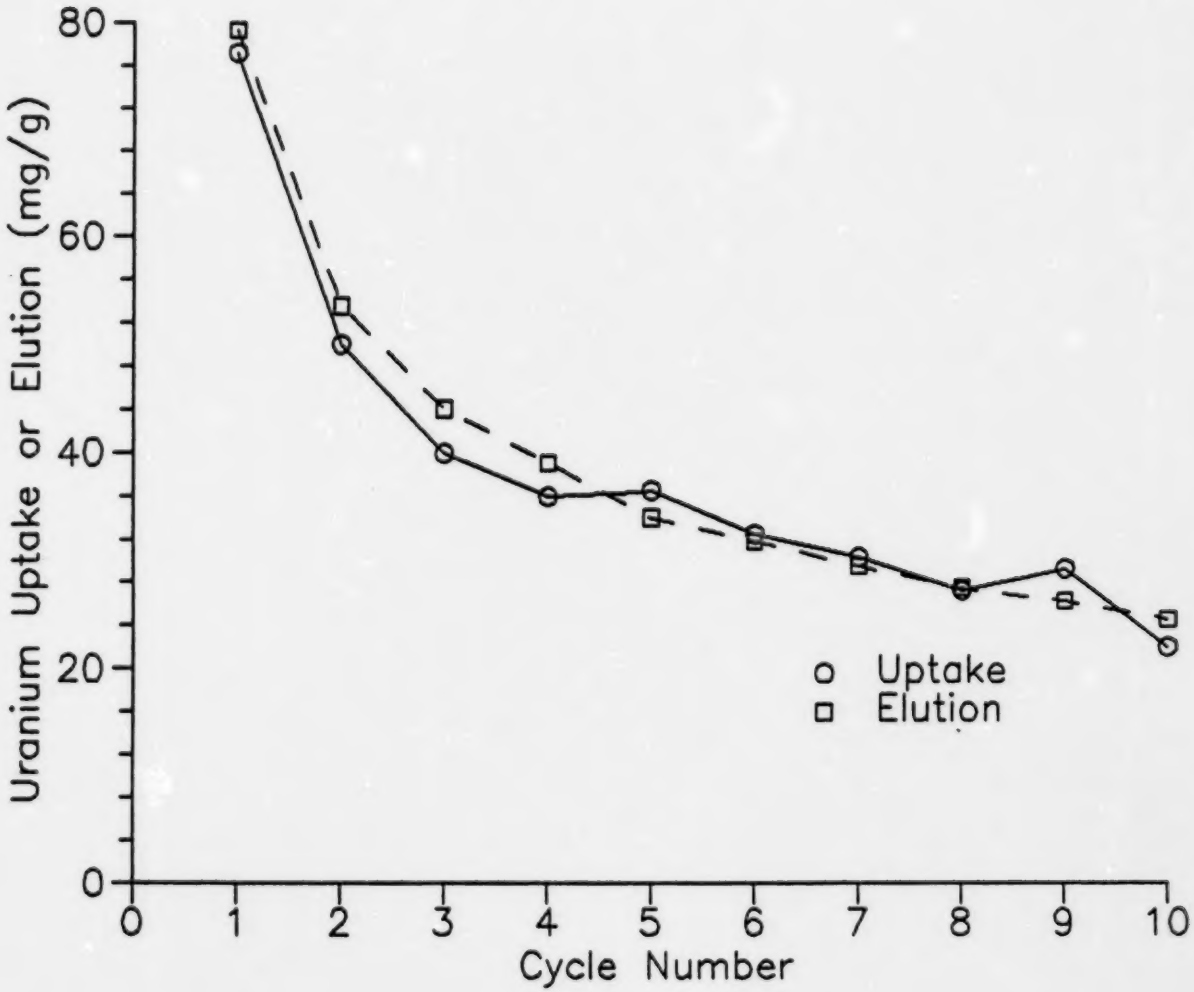

Figure 3.12 Loading–Elution Cycling

total weight loss is loss of biomass and not of additives, the corrected biomass weight loss would be approximately 49%. Since no significant visible loss of biomass was observed during the experiment, some dissolution of biomass components apparently took place. A very small quantity of a gelatinous substance was found on the filters after each cycle. However, the quantities observed are not believed to be great enough to account for the observed weight loss. The loss of biomass could account for a portion, but not all, of the observed reduction in uptake capacity. It appears that a physical or chemical change may occur in the system which causes the progressive reduction in uptake capacity. It has previously been observed that the uptake capacity of nonimmobilized biomass was reduced by pretreatment of the biomass with an acidic (pH = 4.0) solution. The actual mechanism of the uptake reduction phenomenon is not known at this time. Electron microscope studies of the biomass particles after successive loading and elution cycles may elucidate the mechanism responsible for this phenomenon.

3.5 Continuous Column Experiments

3.5.1 Introduction

Ten cycles of loading and elution were carried out in the continuous column experimental system using pH adjusted Solution D as the loading feed solution. In addition, two more cycles were carried out at higher flow rates. A new bioleach solution was used for the additional cycles as a sufficient quantity of Solution D was not available for these tests. Effluent concentration data for the first ten cycles are given in Tables A1 - A4 in the Appendix. These tests were carried out at a flow rate of 1 mL/min. Similar data for tests No. 11 and No. 12 are given in Tables A5 and A6. Test No. 11 was run at a flow rate of 3 mL/min and test No. 12 was run at 6 mL/min. Uranium concentrations of the solution drained from the column at the completion of each run, the collected column effluent, and the column rinse water are given in Tables A7 and A8. The loading breakthrough curves for the first ten cycles are depicted graphically in Figures 3.13 - 3.22. The elution breakthrough curves for the first ten cycles are shown in Figures 3.23 - 3.32. For comparison, the loading breakthrough data

for Cycles 1 and 2 are plotted together in Figure 3.33. In Figure 3.34, the loading breakthrough data for Cycles 2, 5, and 9 are plotted together for comparison. Similarly, elution data for Cycles 2, 5, and 9 are plotted together in Figure 3.35. Loading and elution data for tests No. 11 and No. 12 are shown graphically in Figures 3.36 - 3.39. The loading data for Cycle 1 are incomplete due to a malfunction of the column sampling system. The problem was corrected and complete data sets were collected for all subsequent runs. Although a full set of samples was not obtained for Cycle 1 loading, the run was carried to completion and the final biomass uptake was computed from the concentration of the collected effluent.

3.5.2 Loading

For the first nine cycles, it can be seen from the loading breakthrough curves that the column breakthrough begins when about 1000 mL of solution has passed through the column. This corresponds to a run time of about 17 hours. For Cycles 2 through 9, approximately 65% of the uptake capacity of the biomass was exhausted at the onset of breakthrough. The breakthrough is essentially complete after about 2700 mL of solution has been treated, corresponding to a run time of about 45 hours. Figure 3.33 suggests that the slope of the breakthrough curve for Cycle 1 may be less steep than that of Cycle 2. Comparison of the uranium concentrations of the solutions drained from the column after completion of the 48 hour loading cycles (Table A7) suggests that breakthrough may not have been complete for Cycle 1 after 48 hours. Figure 3.34, which shows loading breakthrough data for Cycles 2, 5, and 9 superimposed on the same graph, suggests that there is little change in the performance of the biosorption column after the first cycle. It is interesting to note that after the first cycle relatively high uranium concentrations were observed initially in the loading effluents. After the passage of around 200 mL, the uranium concentrations were relatively low until the onset of breakthrough. Since care was taken to rinse the sampling system, it does not seem likely that this phenomenon can be attributed to contamination in the sampling system. It appears to be the result of hydraulic short circuiting in the bed. Air bubbles trapped among the bed

particles, slowly aggregated into large ones that bubbled upwards in the immobilized biomass bed, disturbing the hydraulic behaviour of the flow in the reactor and allowing liquid to bypass the reactor.

It can be observed from Figure 3.22 that the breakthrough curve for Cycle 10 is somewhat different than for the previous cycles. The first nine cycles were run on the same feed solution prepared by processing Solution D as previously described. As this solution was used up in the first nine cycles, additional solution was decanted from the tank in which Solution D was originally processed. This decantate was filtered and used as feed for Cycle 10. It was originally thought that this solution would be the same as the feed solution used for the first nine cycles. The process data for Cycle 10, however, indicate that this new solution had a higher uranium concentration than the solution used in the earlier runs. In fact, the solution appeared to have a higher uranium concentration than the original unprocessed bioleach solution from which it came. This solution had been in contact with the precipitate from the pH adjustment process for several weeks. Apparently, during this time some of the uranium in the precipitate redissolved in the supernatant solution. The uranium concentration of the feed solution for Cycle 10 was, therefore, greater than that of the previous cycles. This then accounts for the difference in the Cycle 10 breakthrough curve. From Figure 3.22 it can be seen that the breakthrough began when about 500 mL of solution had been treated as compared with 1000 mL for the previous cycles. The breakthrough appears to be essentially complete after approximately 1500 mL was treated. The breakthrough curve appears to be steeper than for the previous cycles.

Cycles 11 and 12 were run to test the effects of higher flow rates on the performance of the biosorption column. These cycles were run with a different feed solution than the previous cycles. This solution was also prepared from Denison Mines bioleach solution in the same manner as the previous solutions. In this case the bioleach solution had an initial uranium concentration of 182 mg/L and a uranium concentration of 115 mg/L after adjusting the pH to 4. Thus the feed for these last two cycles was considerably weaker than for the

previous cycles. The breakthrough curve for Cycle 11 (3 mL/min) is shown in Figure 3.36. It can be seen that breakthrough began when about 1000 mL of solution had been treated and was completed after about 8000 mL had passed through the column. The slope of the breakthrough curve is more gradual than for the previous cycles. This may be the result of the lower uranium concentration and also the higher flow rate. For Cycle 12 (6 mL/min) (Figure 3.37), the column effluent uranium concentration remained always high. Because of the high flow rate and the limited biomass bed depth, the uranium removal rate was limited and did not alter substantially the uranium feed concentration, leading to a rapid break through. In this case the breakthrough curve is very flat. The scatter in the data may be due to a combination of experimental error and variations in the effluent caused by the high flow rate. The effects of higher flow rates could be better investigated using a larger column. In the small experimental column the adsorption zone is wider than the depth of the adsorbent bed and thus it is not possible to observe the movement of the adsorption zone through the column.

Table 3.11 gives the total uranium uptake per gram of biomass after each loading cycle. The uptake was calculated from a mass balance using the concentration of the collected effluent, the feed concentration, and the volume treated. Table 3.11 also shows the quantity of uranium eluted per gram of biomass in each cycle, also determined by mass balance. It can be seen that the loading is reduced by approximately 25% between Cycles 1 and 2 but that smaller variations in uptake occur between Cycle 2 and subsequent cycles. After the third cycle the uptake appears to be stable at slightly less than 50 mg/g. Although a less concentrated feed solution was used for Cycles 11 and 12, the loading is consistent with the previous cycles. It appears that the higher flow rates did not have any effect on the uptake capacity of the column. The behaviour observed in the continuous column tests is different than that observed in the batch loading-elution cycling experiment where after ten cycles, the observed uranium uptake capacity of the immobilized biomass appeared to drop to about 30% of the original capacity. In the continuous column experiments, the uptake capacity of the biomass

remained over 60% of the original capacity after twelve cycles. In the batch experiment it was observed that a loss of biomass weight occurred over the course of ten cycles which could account for a portion, but not all, of the uptake capacity reduction (Section 3.4). If the uptake capacity after ten cycles in the batch experiment is corrected for the observed weight loss, an uptake of approximately 43 mg/g is obtained. This value corresponds reasonably well with the observed uptake in the continuous column experiment. Possibly the weight loss of the biomass in the batch experiments was partly due to physical damage to the biomass caused by the extended periods of mechanical agitation. The results of the continuous column experiments are encouraging in that the uptake capacity appears to stabilize after the second cycle.

TABLE 3.11: CONTINUOUS COLUMN LOADING AND ELUTION RESULTS

Cycle	Uptake (mg/g)	Elution (mg/g)	%Eluted
1	71.8	71.3	99
2	54.0	53.8	100
3	51.8	46.7	90
4	47.9	44.9	94
5	45.7	45.2	99
6	48.2	43.3	90
7	43.6	42.7	98
8	49.0	44.7	91
9	49.3	39.8	81
10	43.2	28.6	66
11	55.4	49.1	89
12	44.7	42.8	96

3.5.3 Elution

With one exception, the results given in Table 3.11 indicate that a high percentage of the uranium adsorbed on the biomass during each loading cycle was removed by the elution process. This is in agreement with the results of the batch loading-elution cycle tests. The reason for the apparently low elution fraction in Cycle 10 is not known. This condition did not appear to persist as the elution in Cycles 11 and 12 appear to be normal. From the elution breakthrough curves for Cycles 1 through 10 it can be seen that the elution was essentially complete after approximately 400 mL of eluant had passed through the column. This corresponds to a run time of approximately 7 hours. For Cycles 1 and 3 a peak uranium concentration of approximately 5000 mg/L was observed in the eluant. Since the first eluant sample was taken when approximately 55 mL had passed through the column, the actual peak concentration was likely higher. For Cycle 2 the peak uranium concentration was slightly above 4000 mg/L. For Cycles 4 through 9, the observed peak concentrations were between 2000 and 4000 mg/L. The peak concentration for Cycle 10 was slightly below 2000 mg/L. The observed peak concentrations for Cycles 11 and 12 were somewhat lower. Since these cycles were run at higher flow rates, lower eluant concentrations would be expected. In general, the elution process appears to be less efficient at the higher flow rates, requiring a larger eluant volume to complete the elution. This effect is more pronounced at 6 mL/min than at 3 mL/min.

No attempt was made in these experiments to optimize the elution process. It should be possible, in a large scale operation, to optimize the elution process to produce a low volume, high concentration eluate to maximize uranium recovery efficiency while minimizing elution costs. This could be done by proper selection of the sodium bicarbonate concentration, eluant volume, and flow rate.

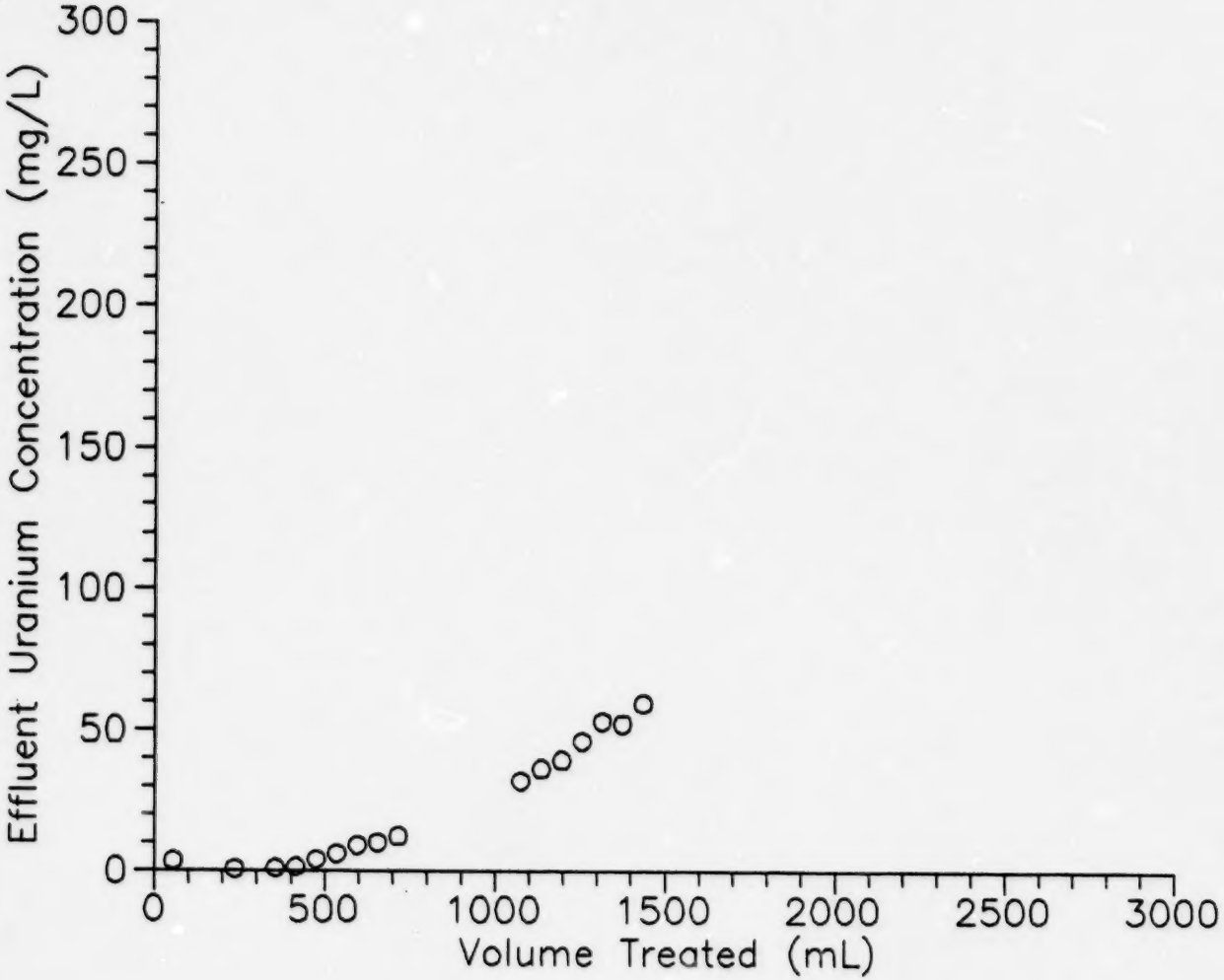

Figure 3.13 Loading Breakthrough Curve (Cycle 1)

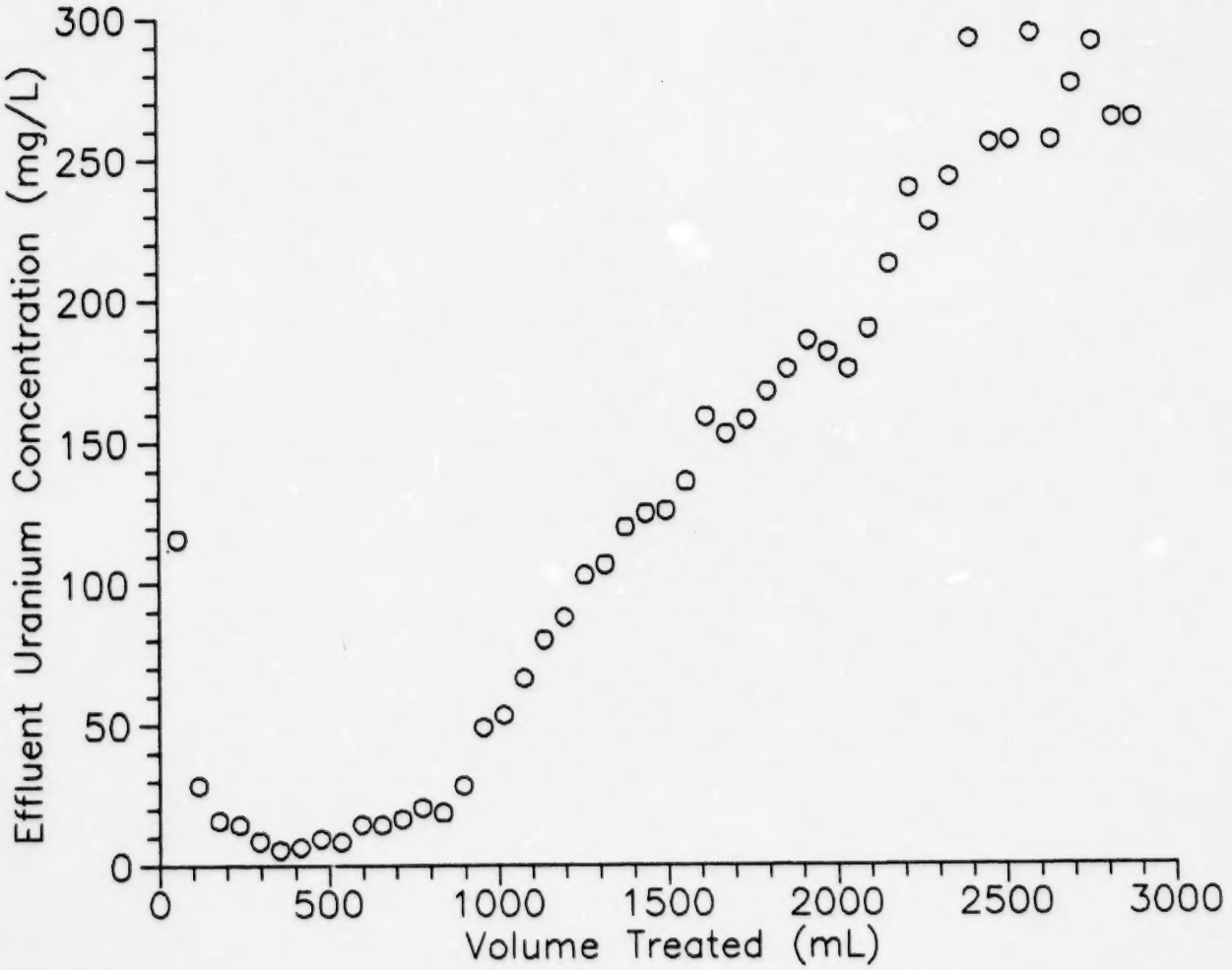

Figure 3.14 Loading Breakthrough Curve (Cycle 2)

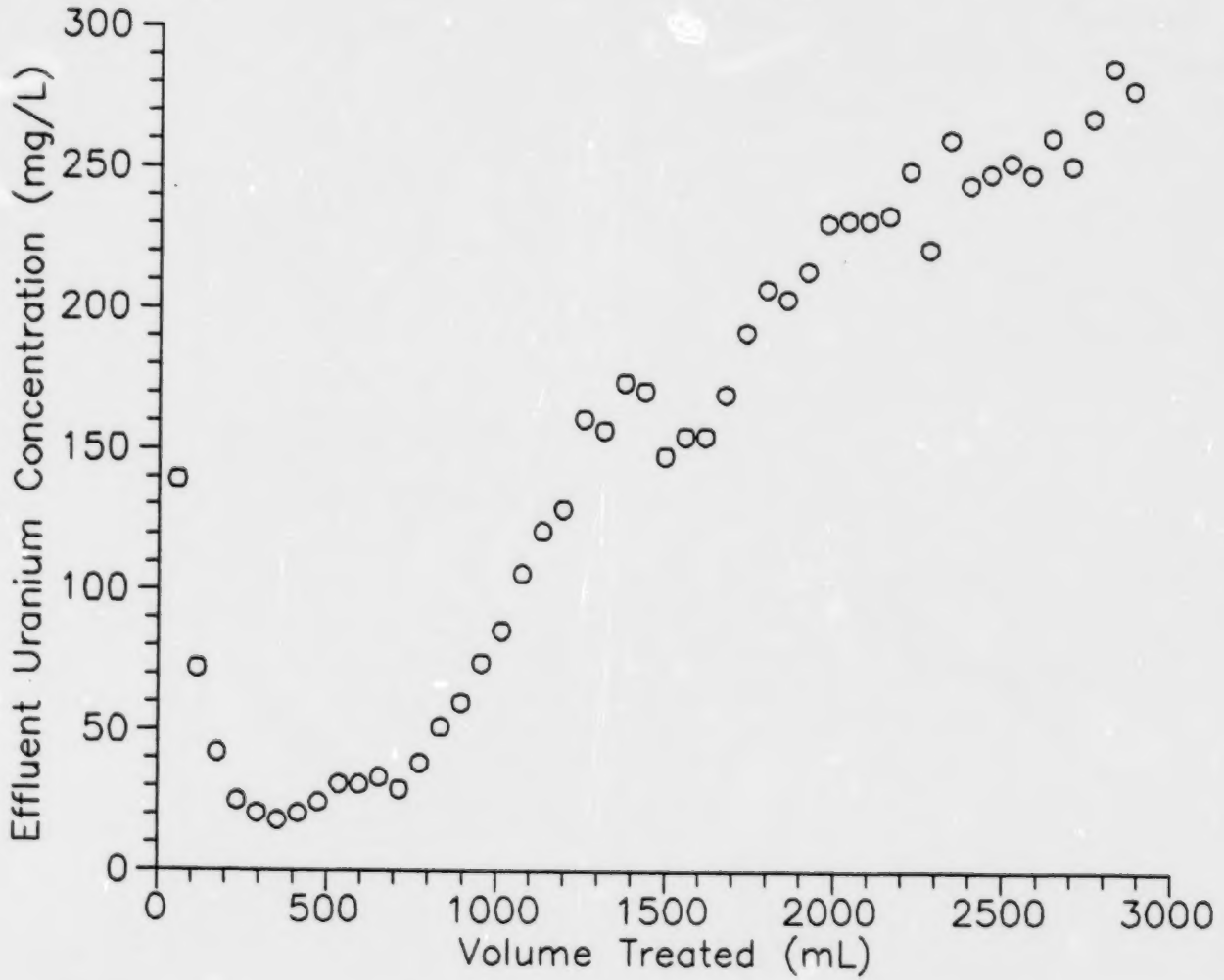

Figure 3.15 Loading Breakthrough Curve (Cycle 3)

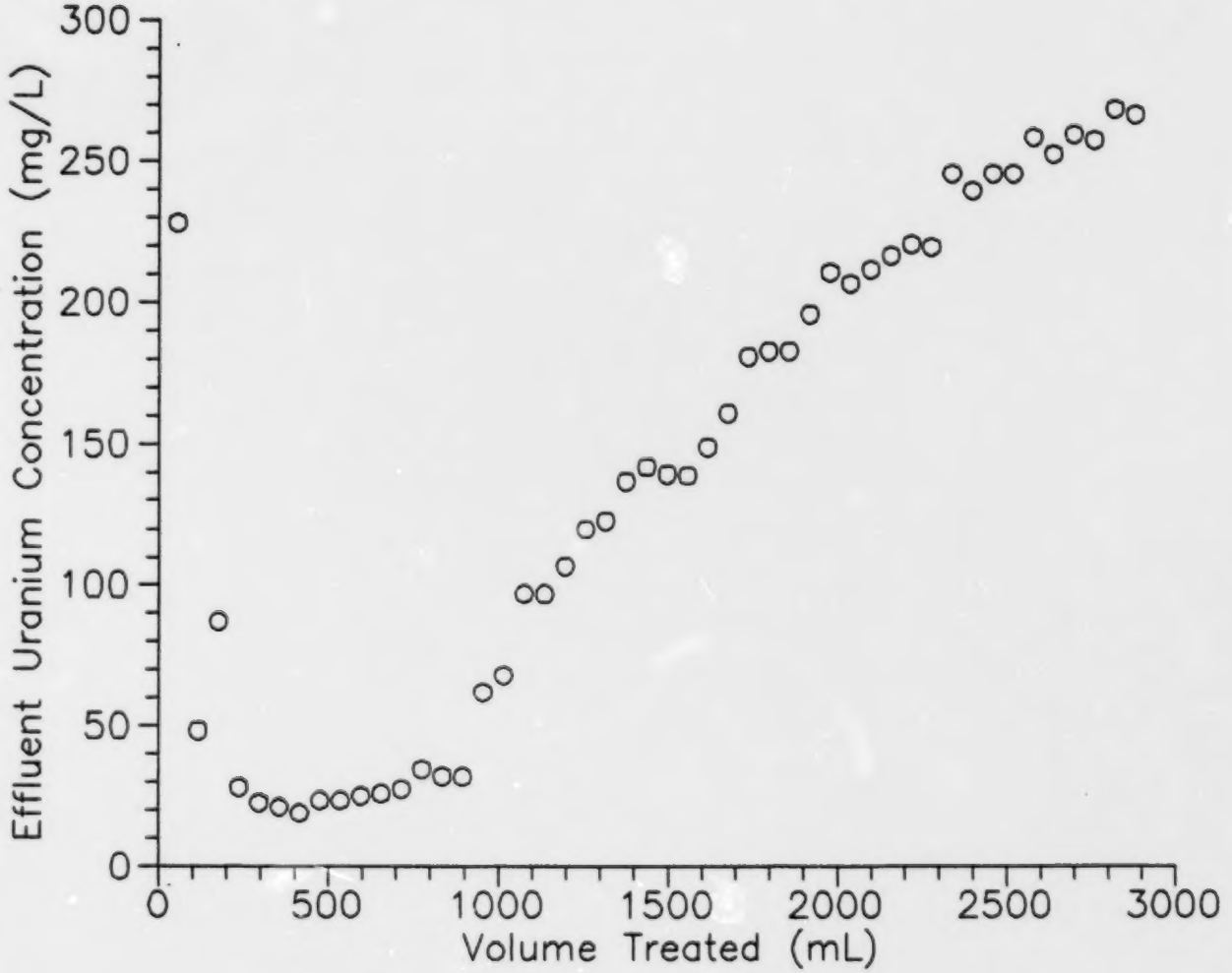

Figure 3.16 Loading Breakthrough Curve (Cycle 4)

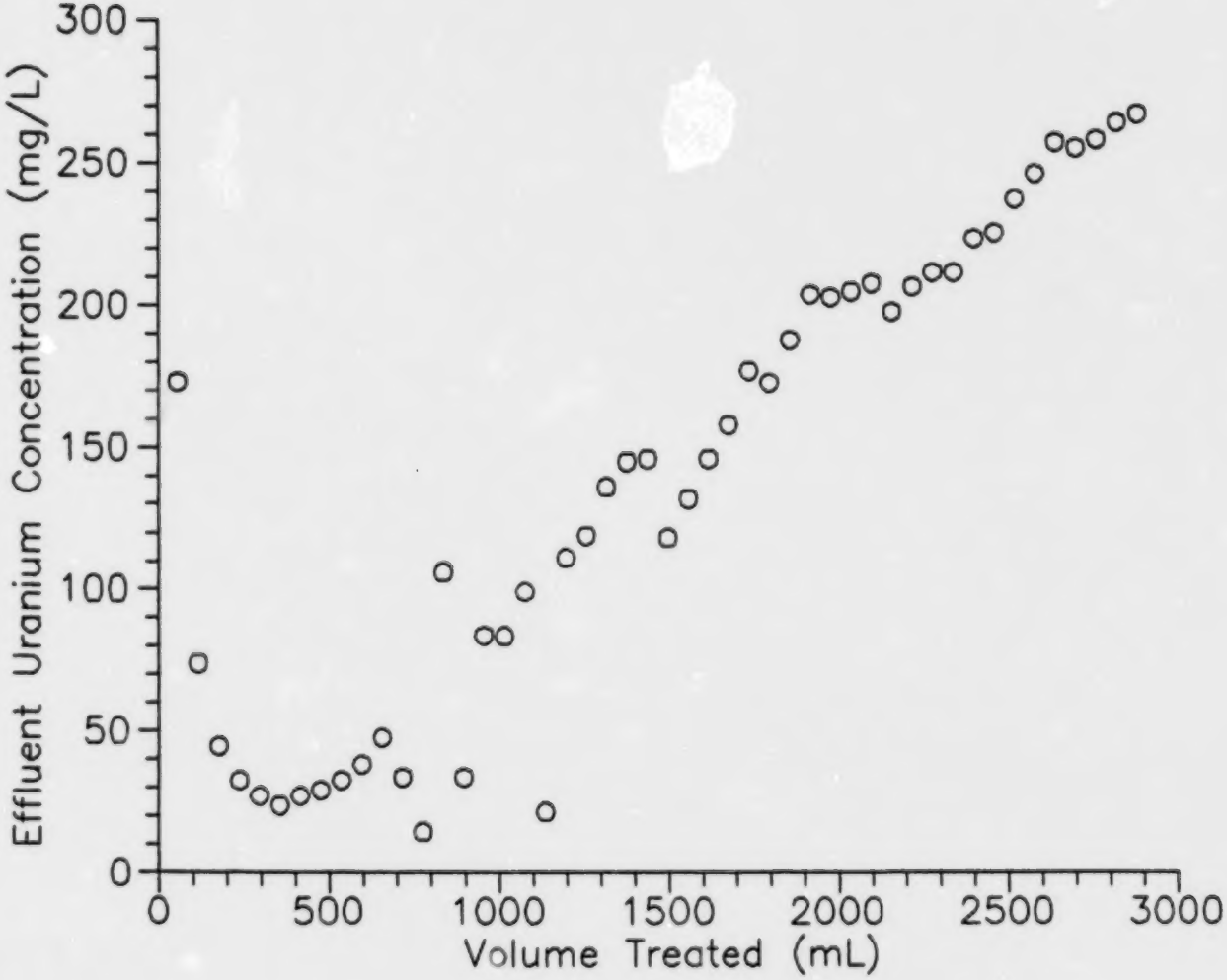

Figure 3.17 Loading Breakthrough Curve (Cycle 5)

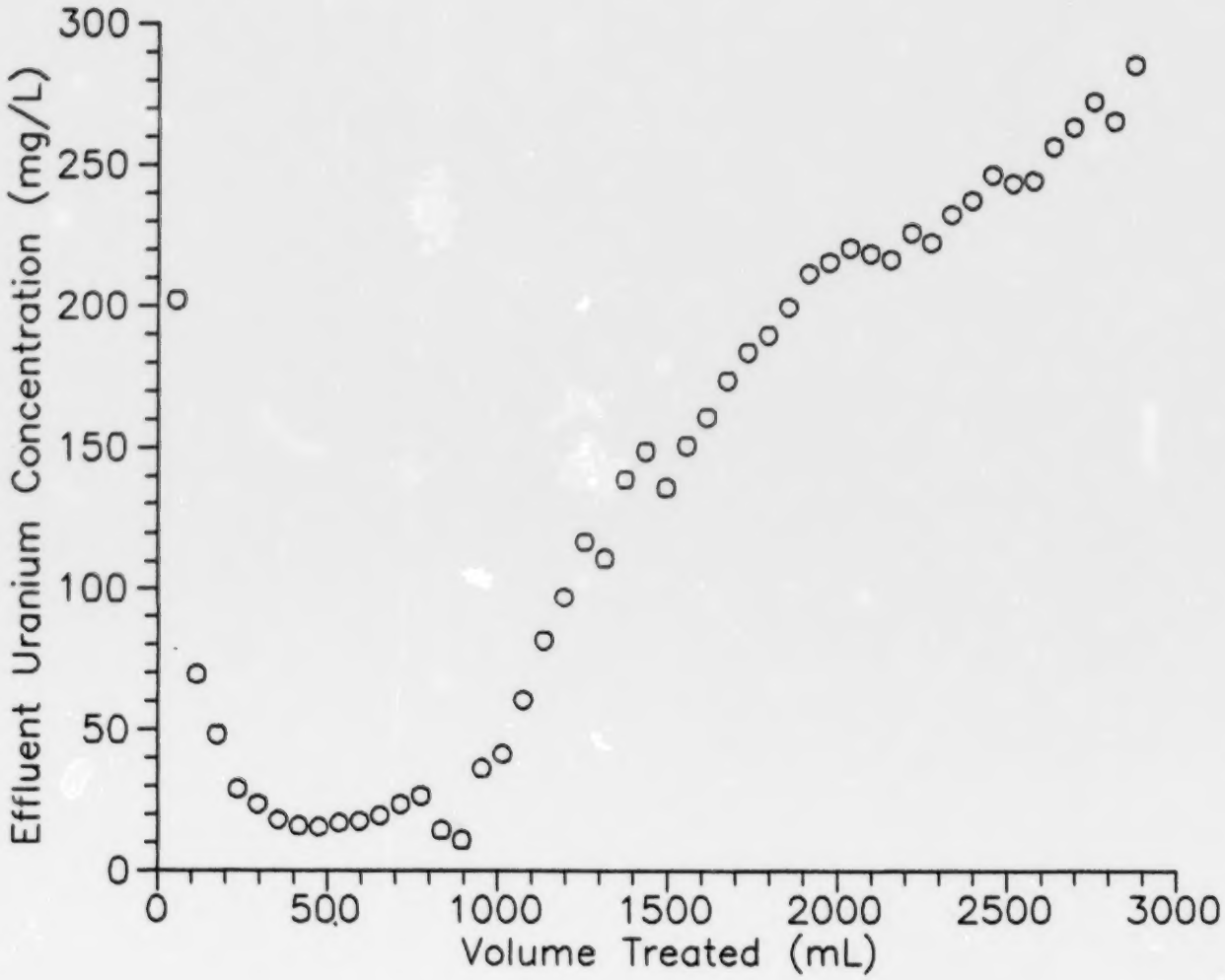

Figure 3.18 Loading Breakthrough Curve (Cycle 6)

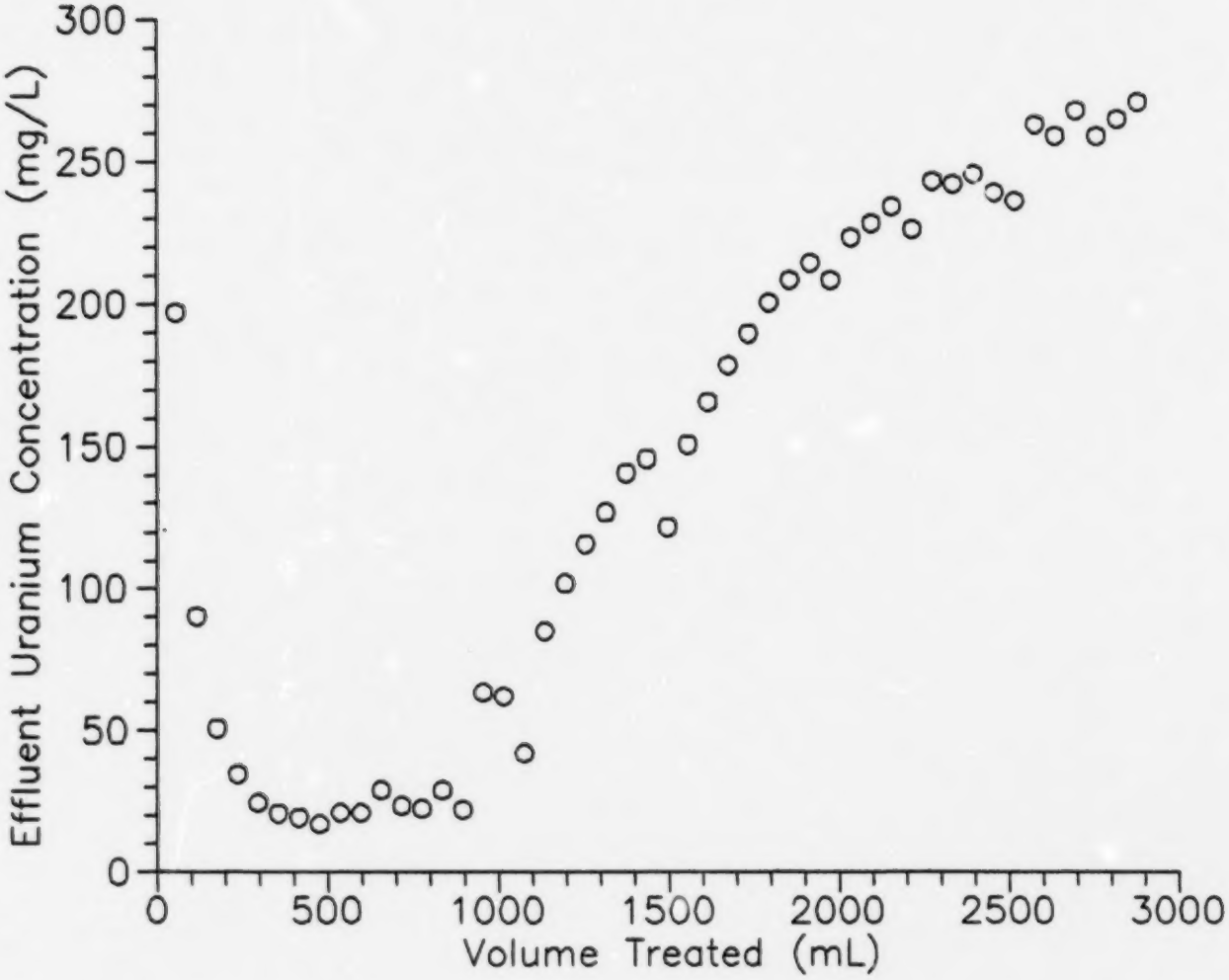

Figure 3.19 Loading Breakthrough Curve (Cycle 7)

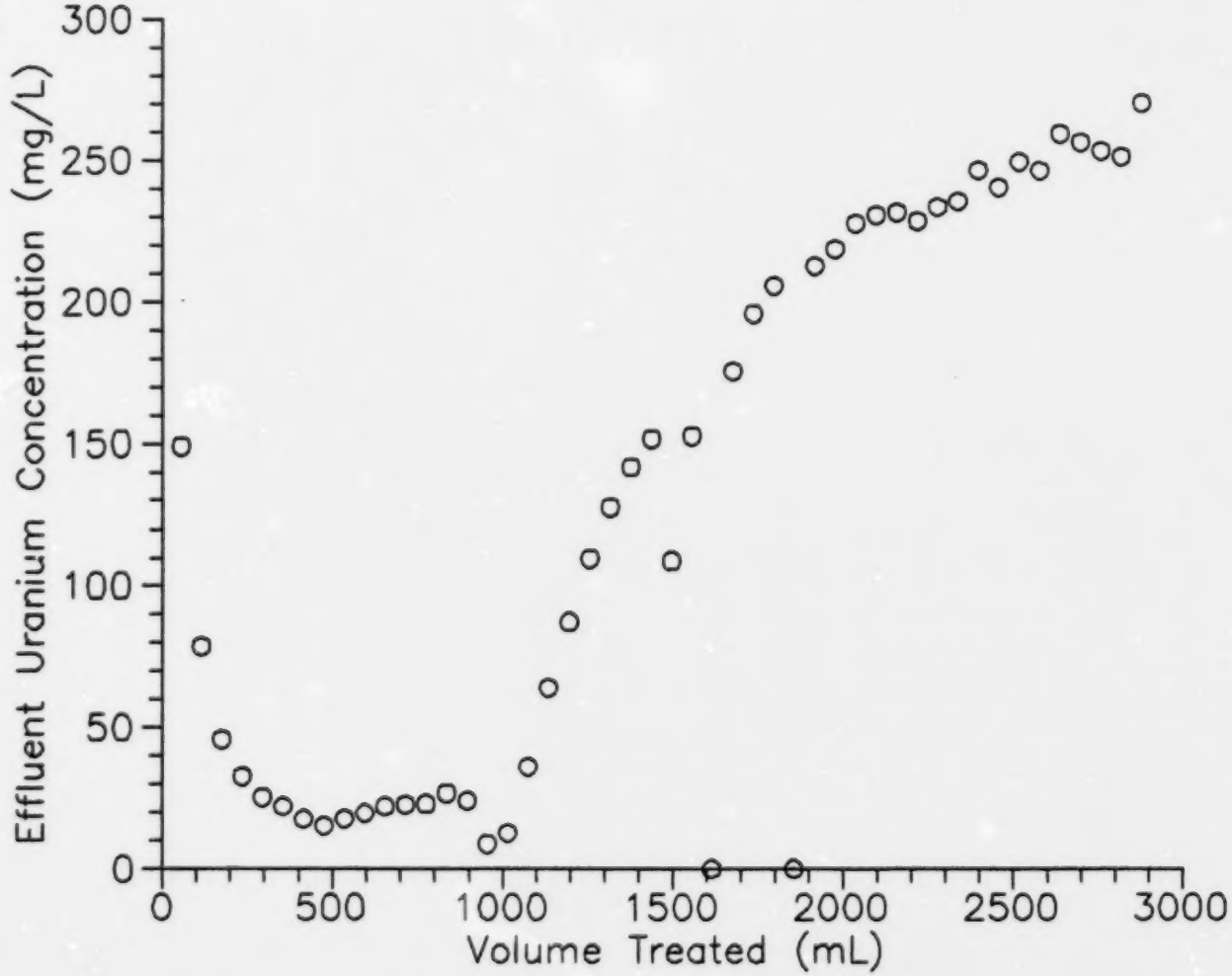

Figure 3.20 Loading Breakthrough Curve (Cycle 8)

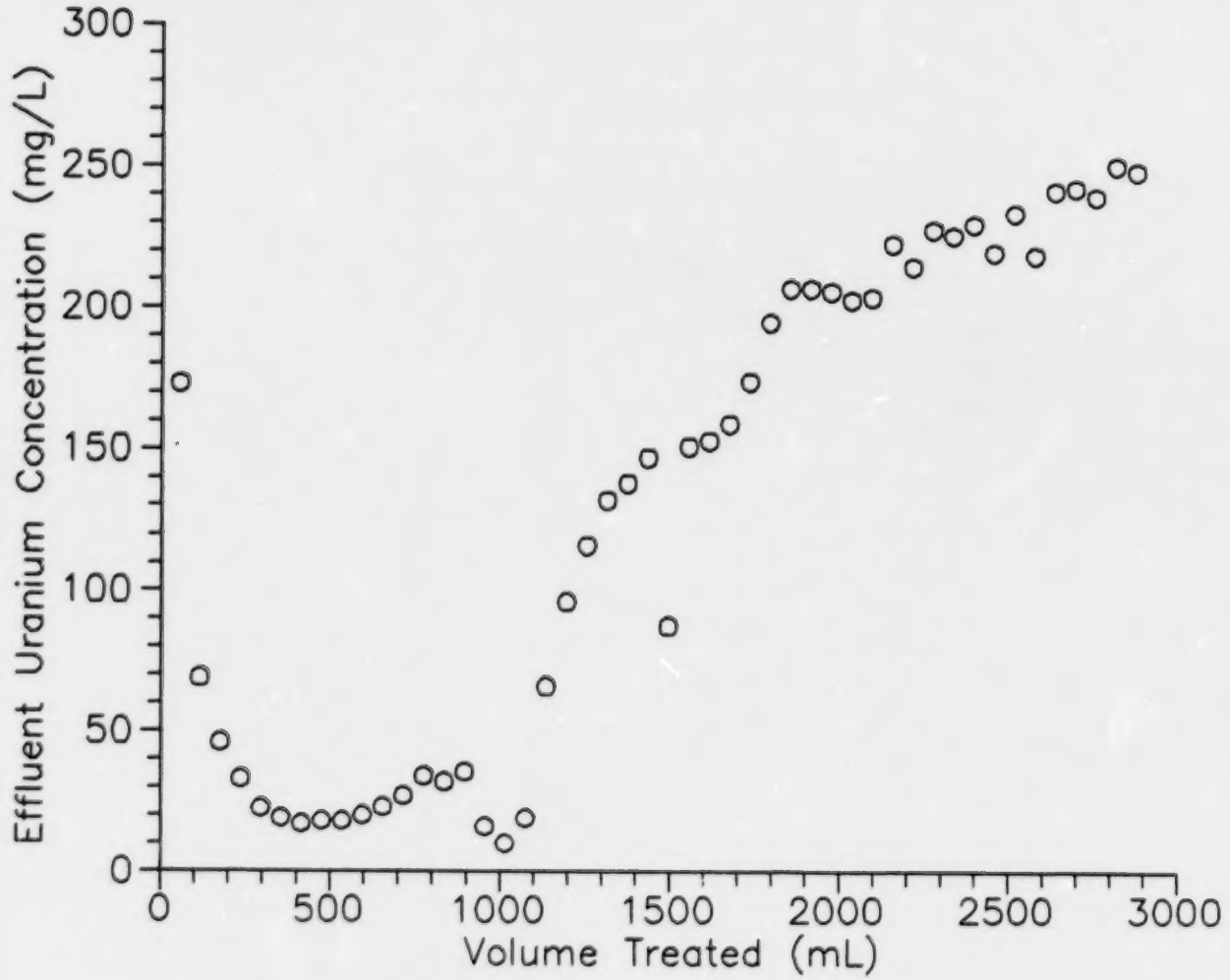

Figure 3.21 Loading Breakthrough Curve (Cycle 9)

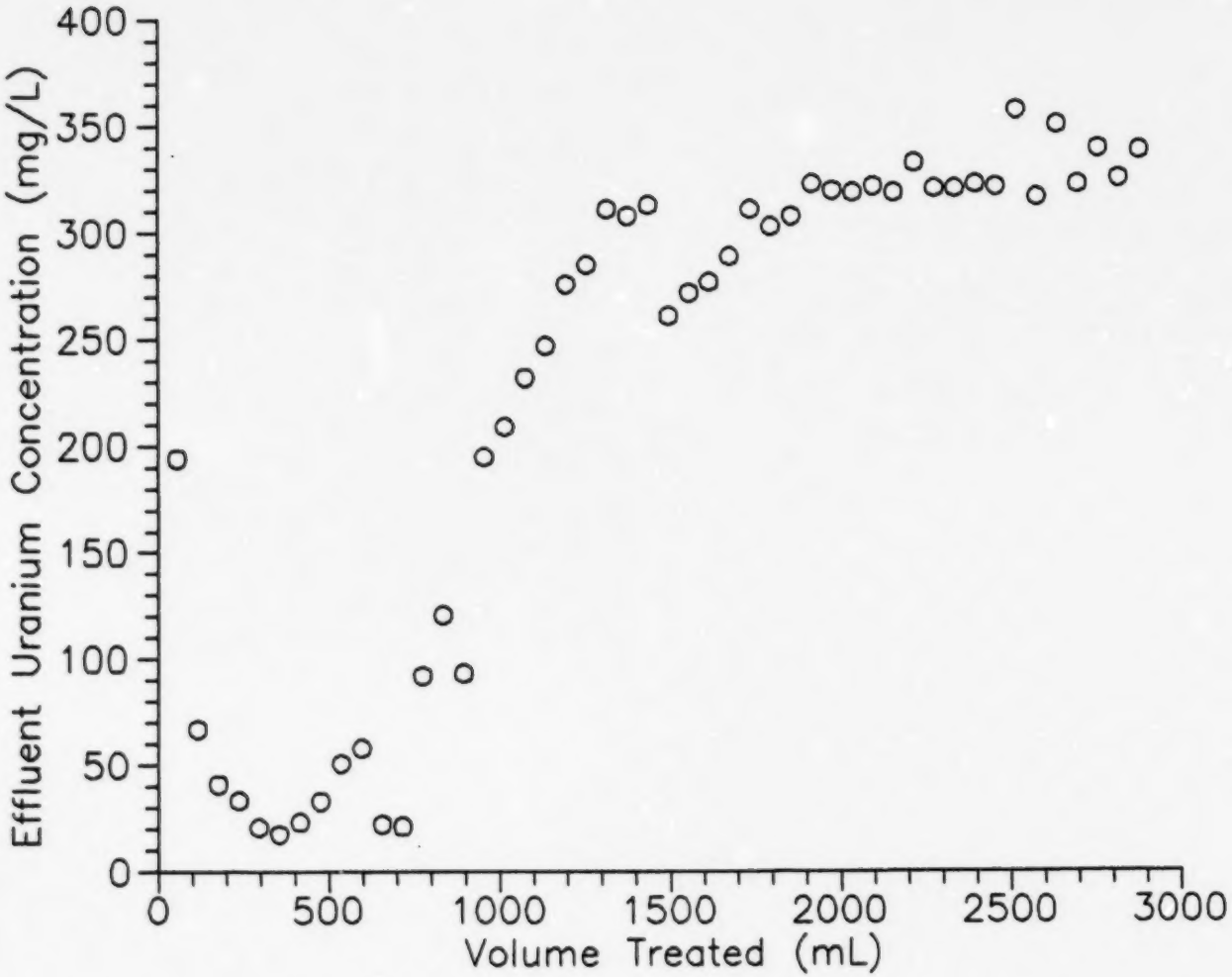

Figure 3.22 Loading Breakthrough Curve (Cycle 10)

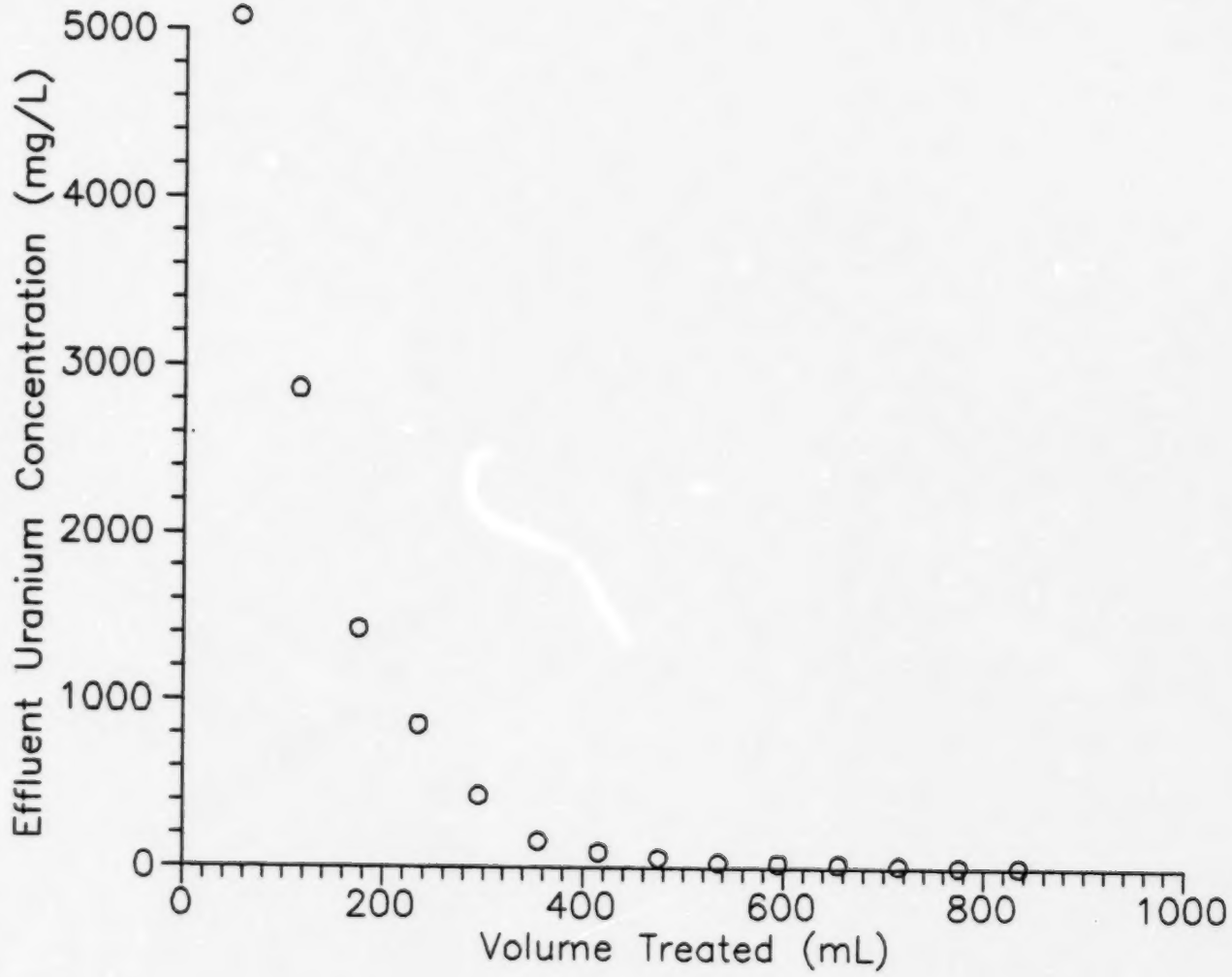

Figure 3.23 Elution Breakthrough Curve (Cycle 1)

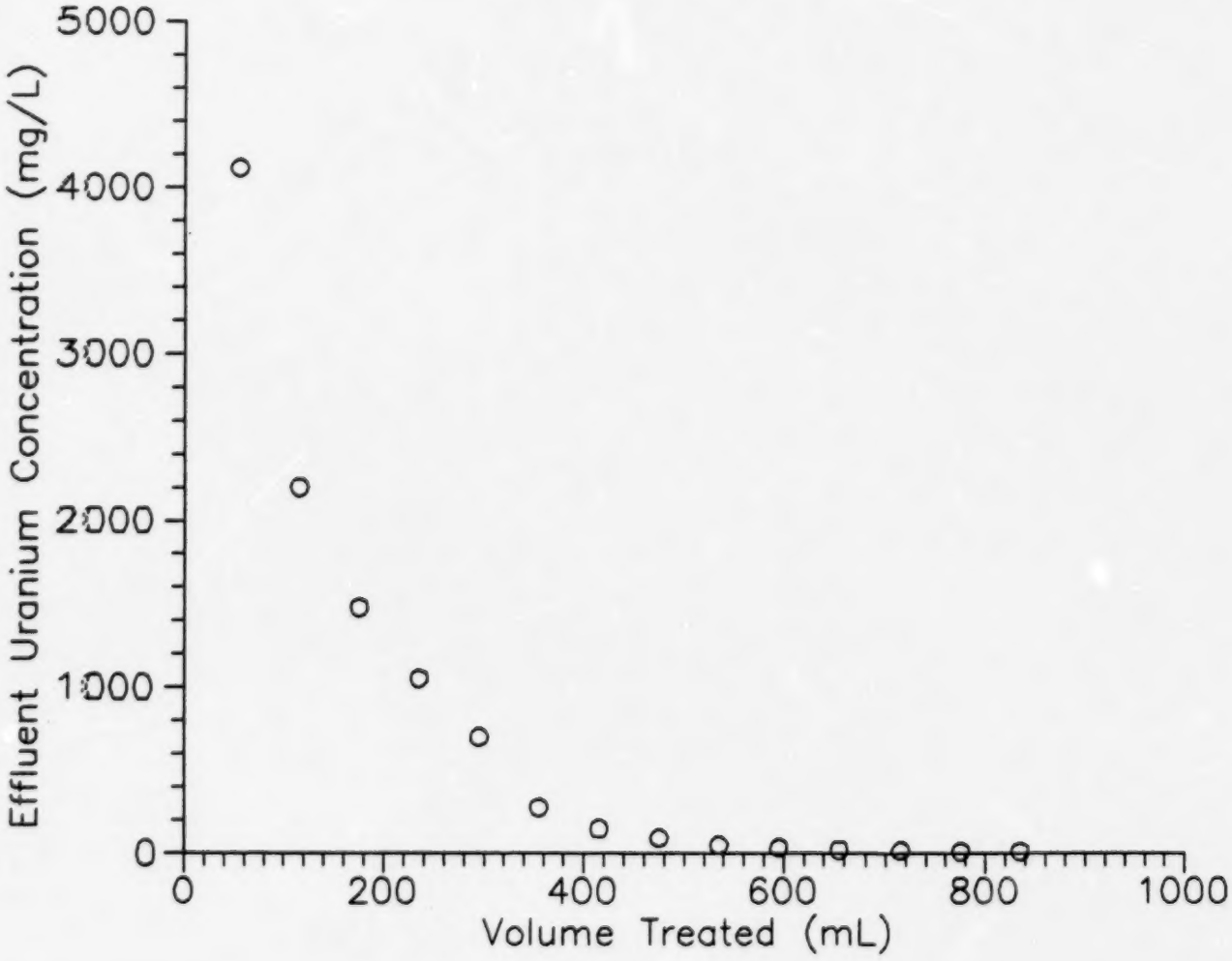

Figure 3.24 Elution Breakthrough Curve (Cycle 2)

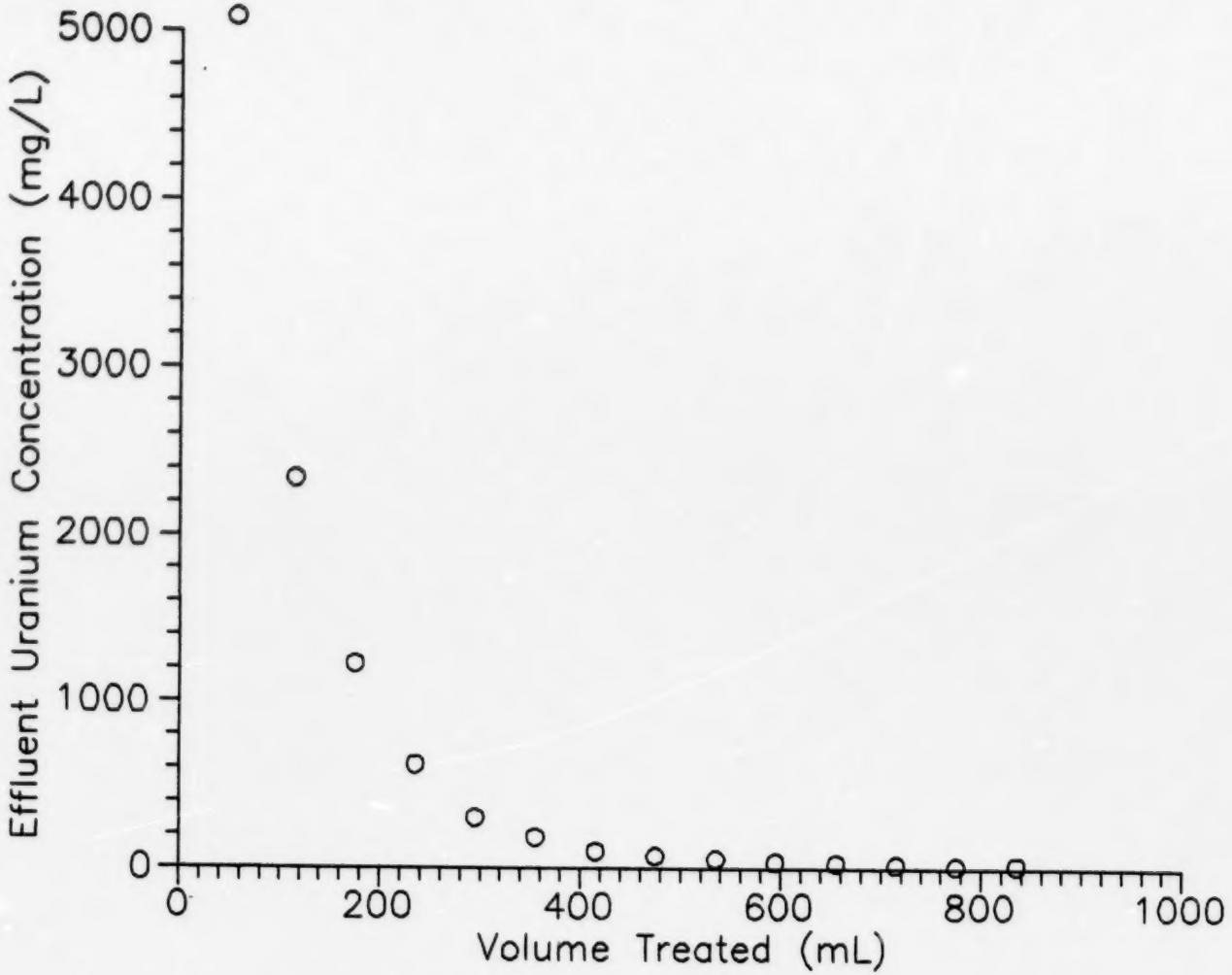

Figure 3.25 Elution Breakthrough Curve (Cycle 3)

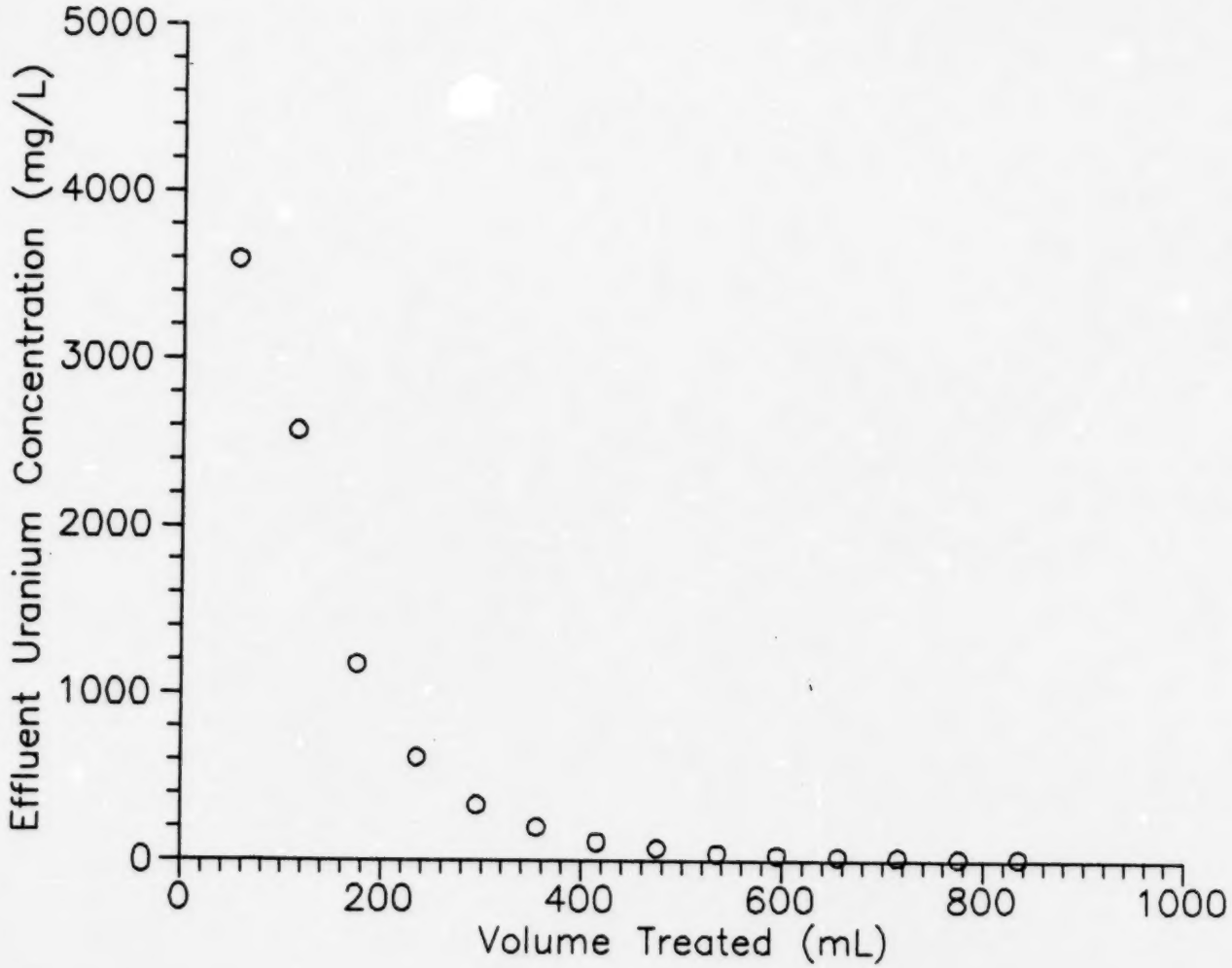

Figure 3.26 Elution Breakthrough Curve (Cycle 4)

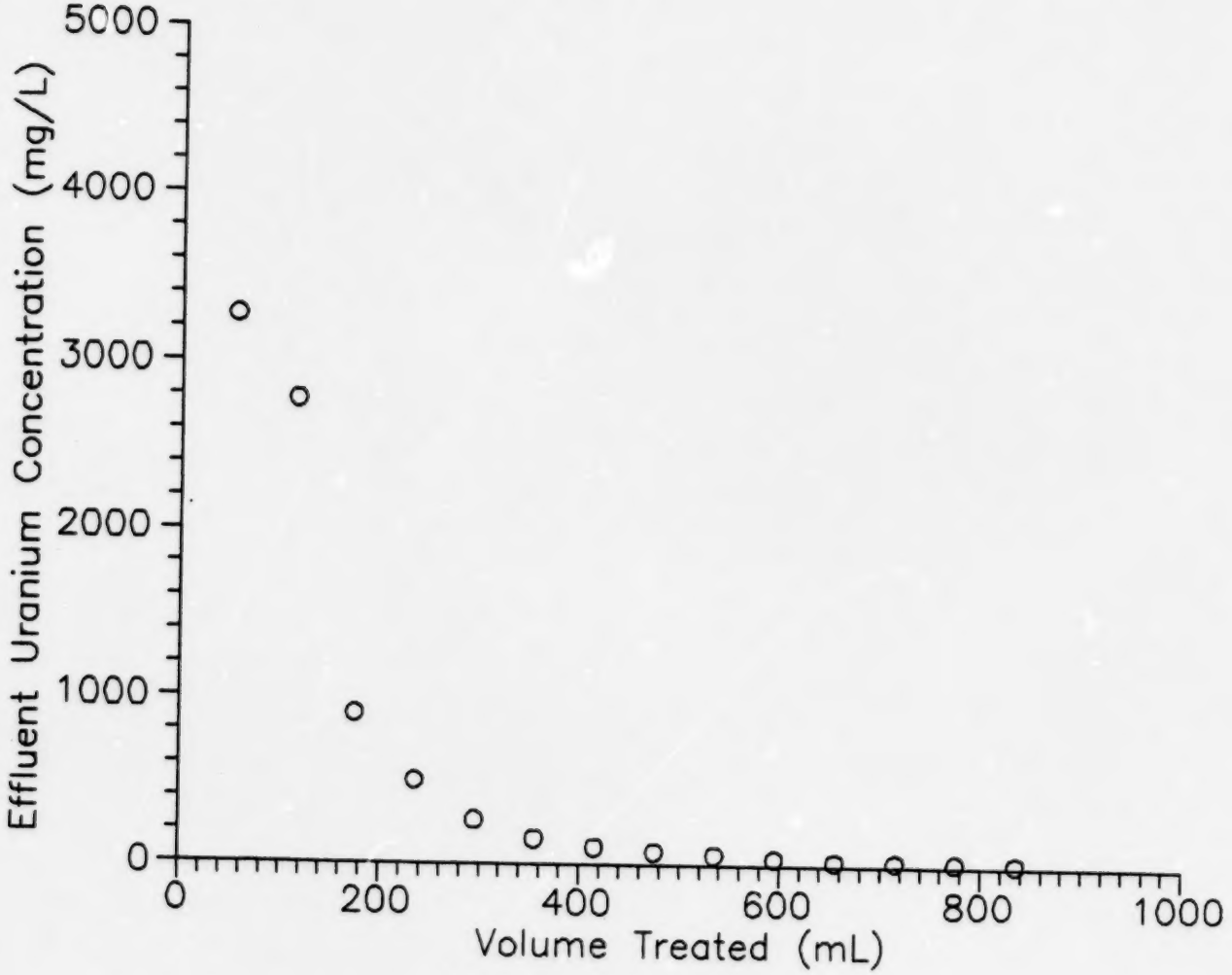

Figure 3.27 Elution Breakthrough Curve (Cycle 5)

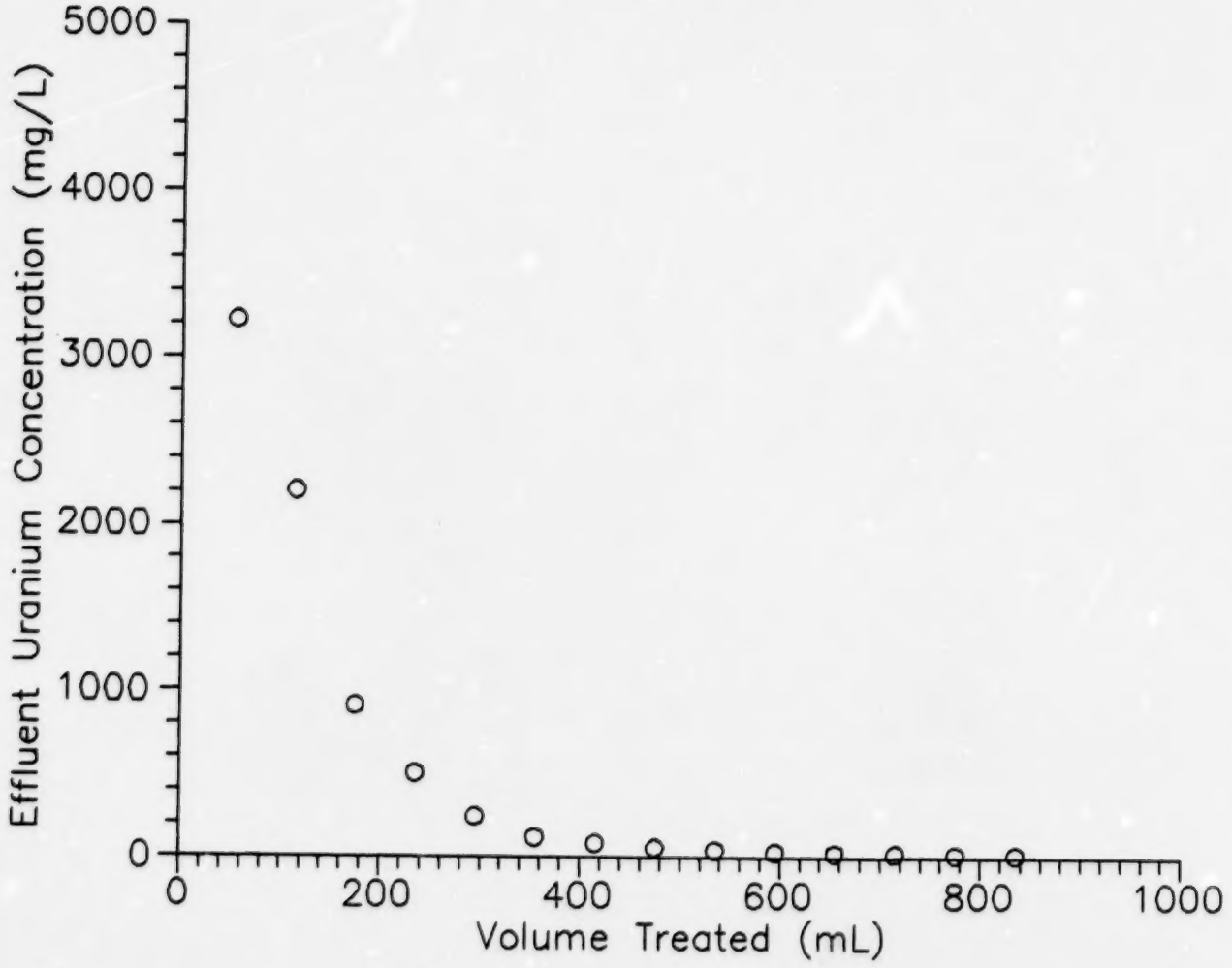

Figure 3.28 Elution Breakthrough Curve (Cycle 6)

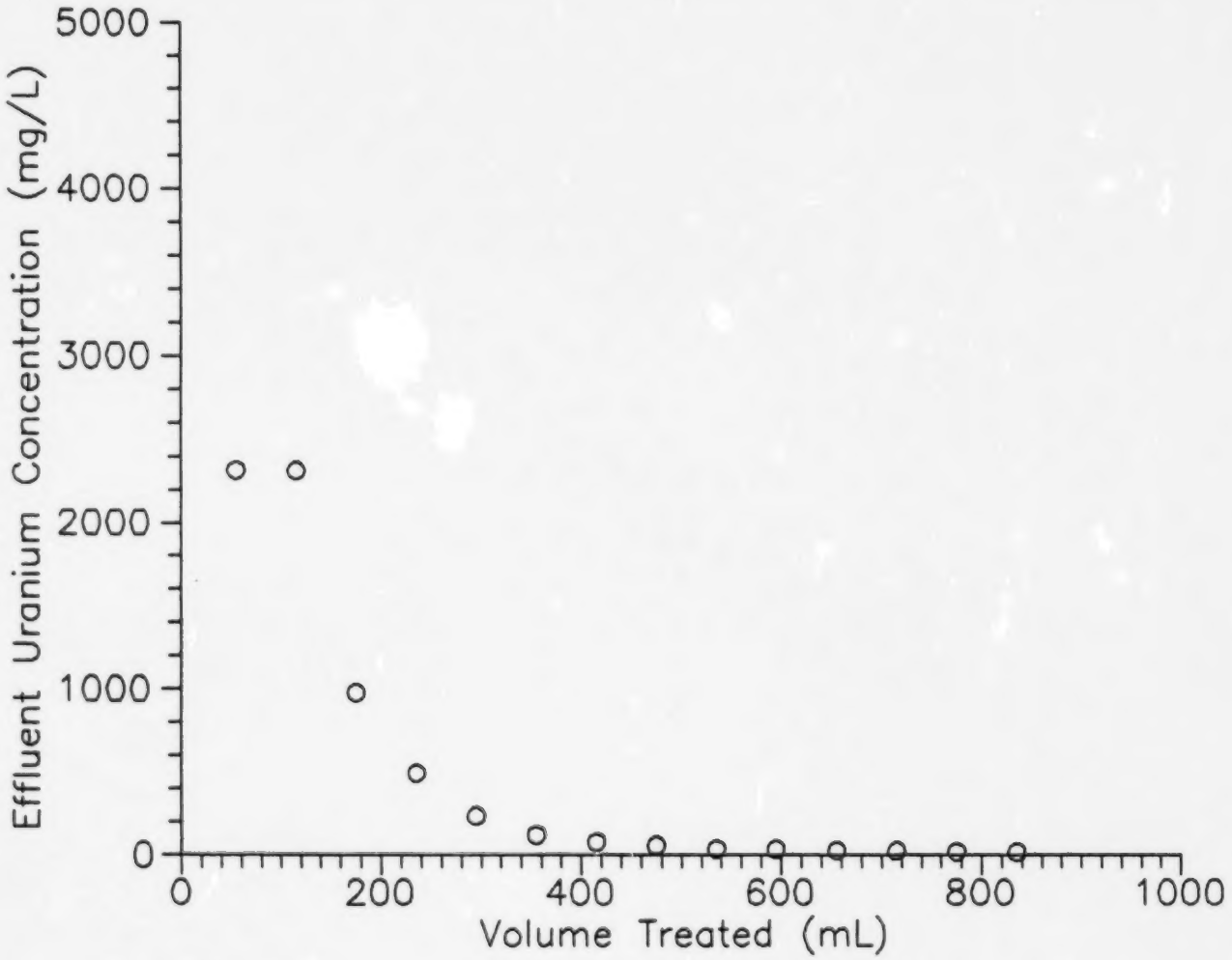

Figure 3.29 Elution Breakthrough Curve (Cycle 7)

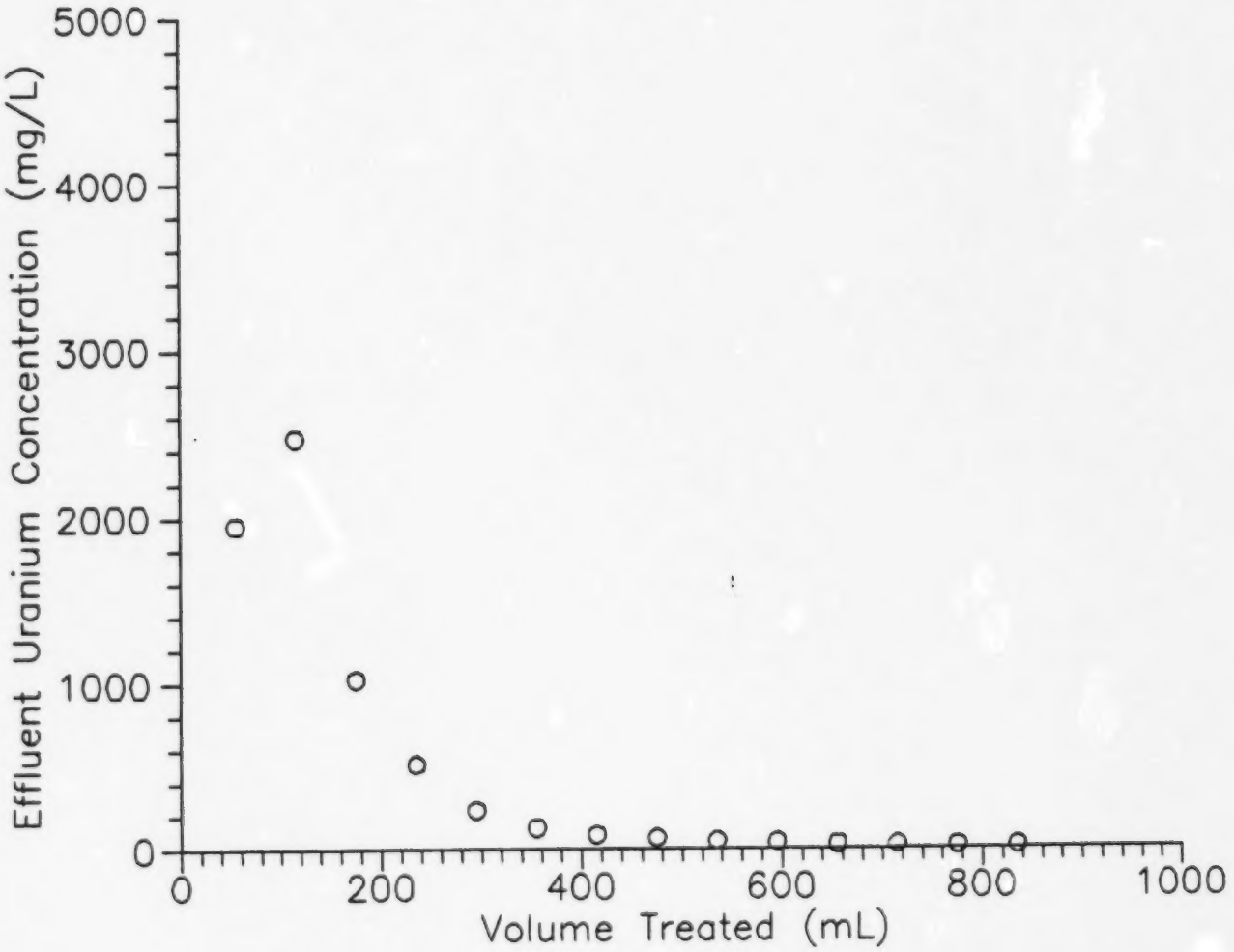

Figure 3.30 Elution Breakthrough Curve (Cycle 8)

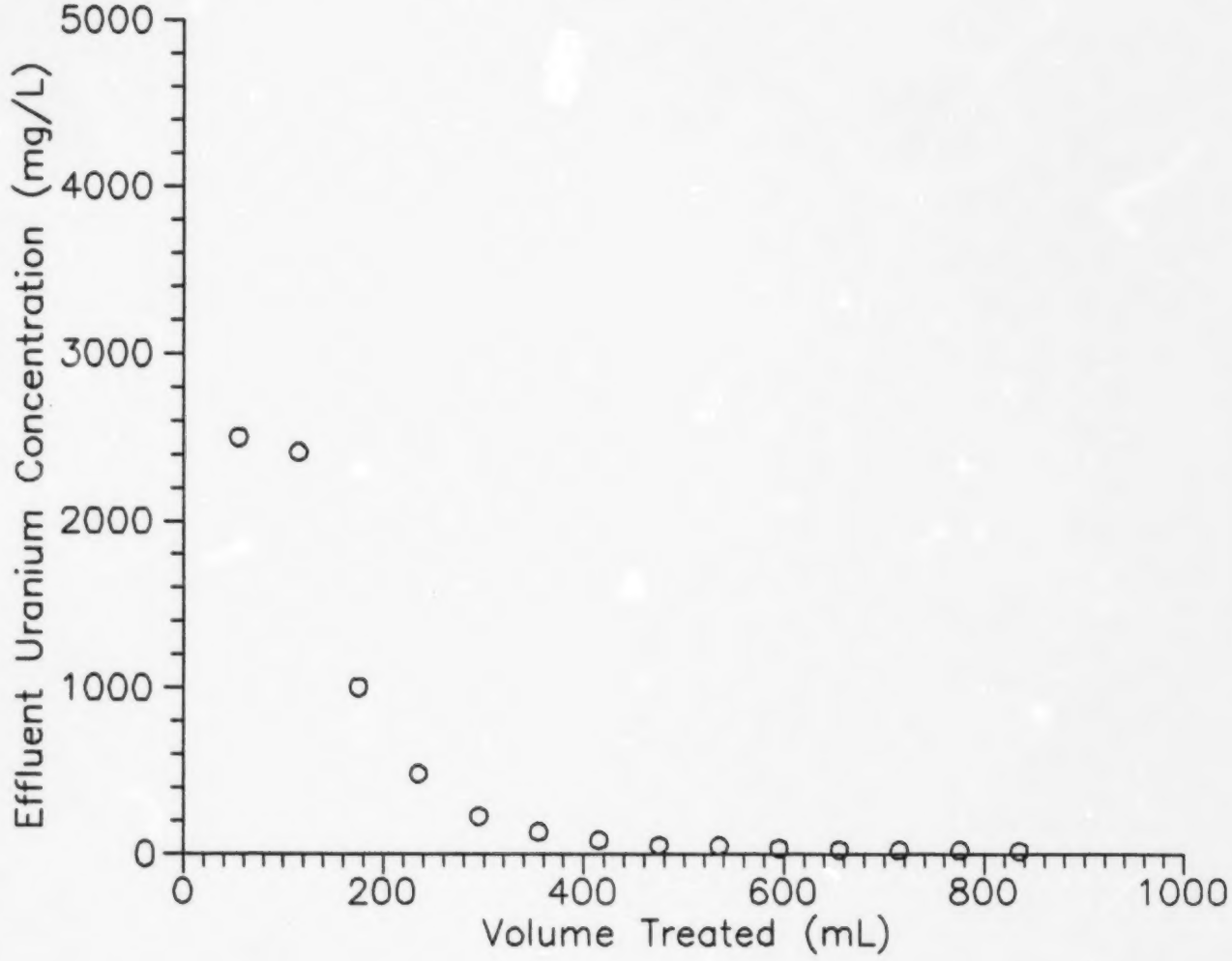

Figure 3.31 Elution Breakthrough Curve (Cycle 9)

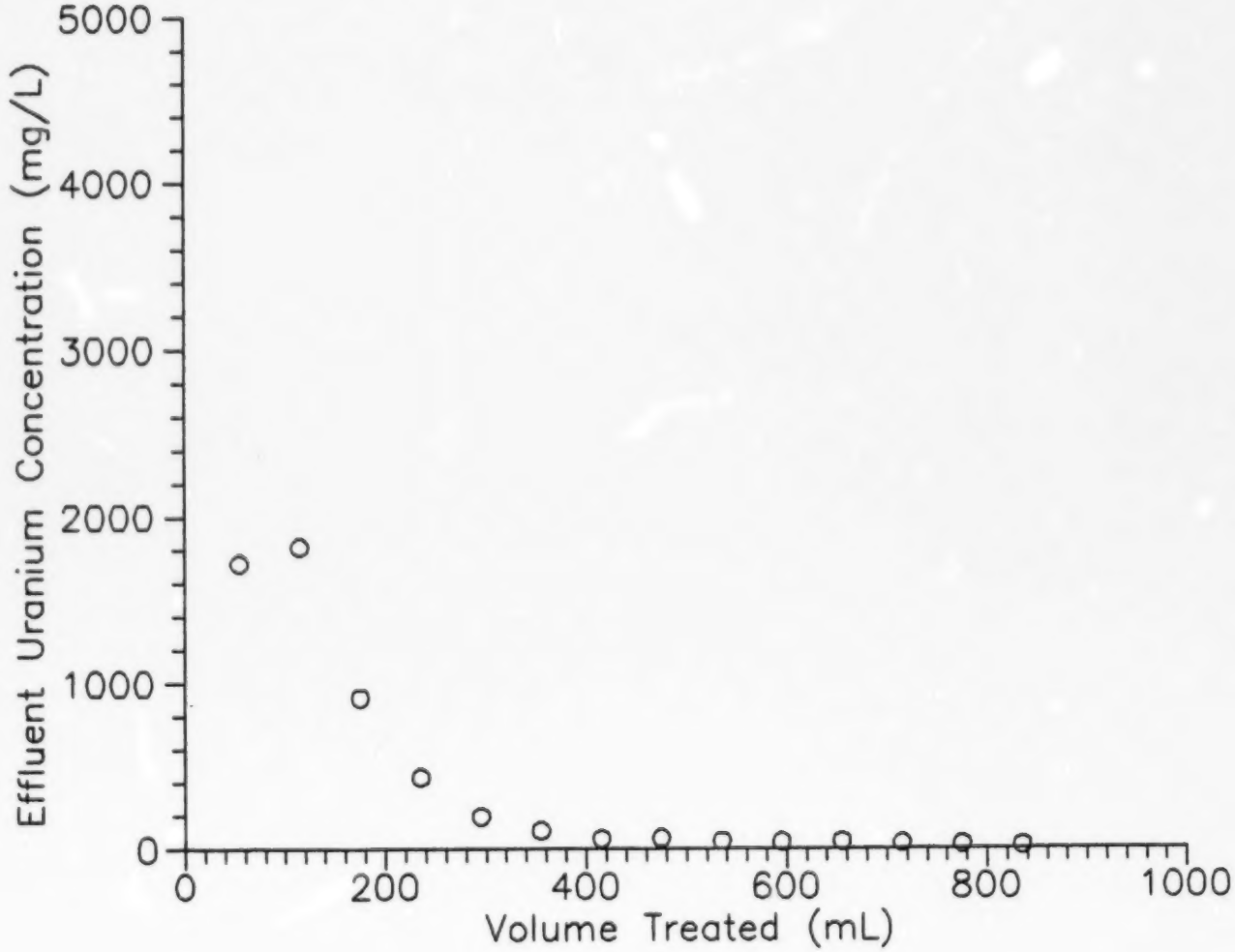

Figure 3.32 Elution Breakthrough Curve (Cycle 10)

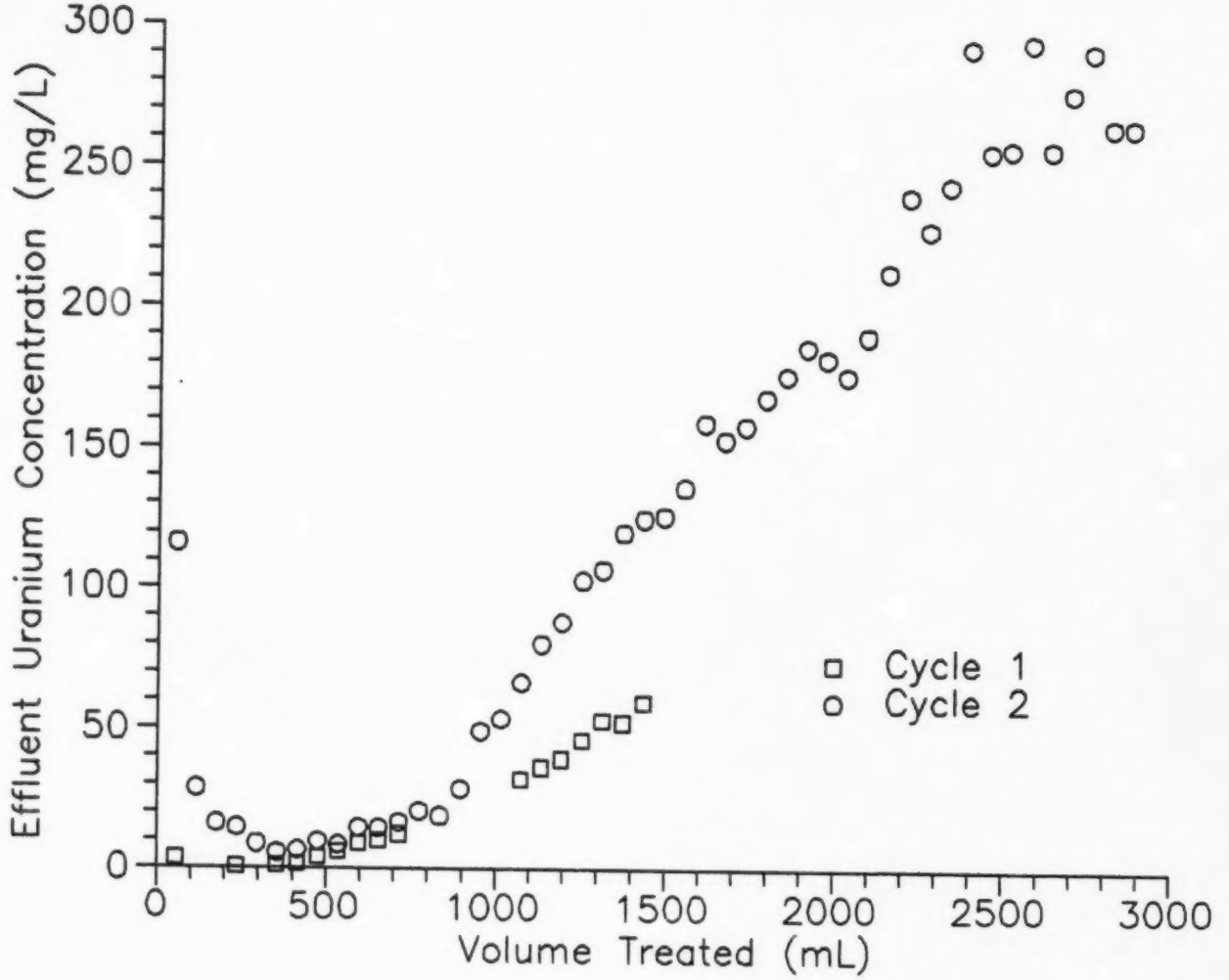

Figure 3.33 Loading Breakthrough Curves (Cycles 1 and 2)

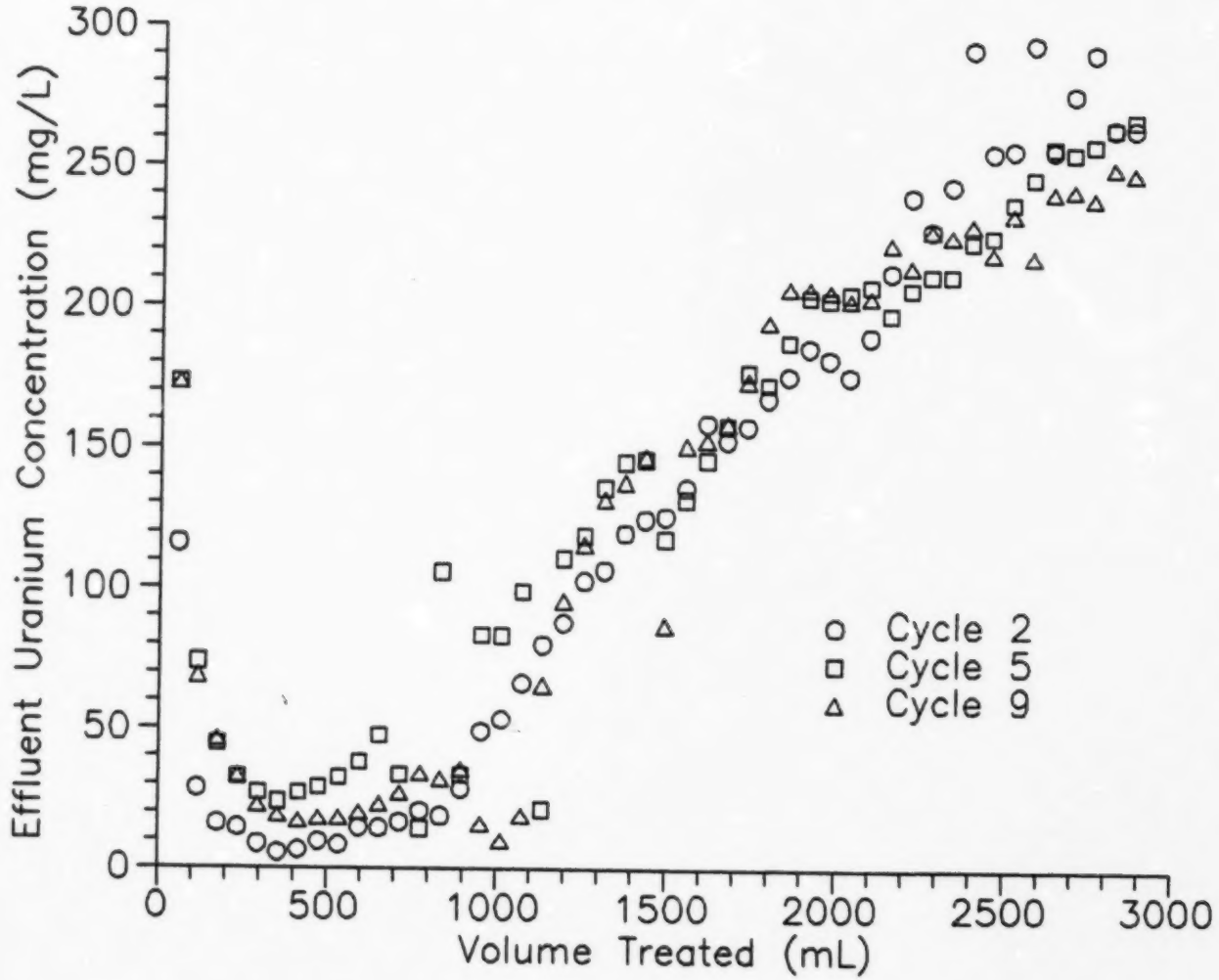

Figure 3.34 Loading Breakthrough Curves (Cycles 2, 5, and 9)

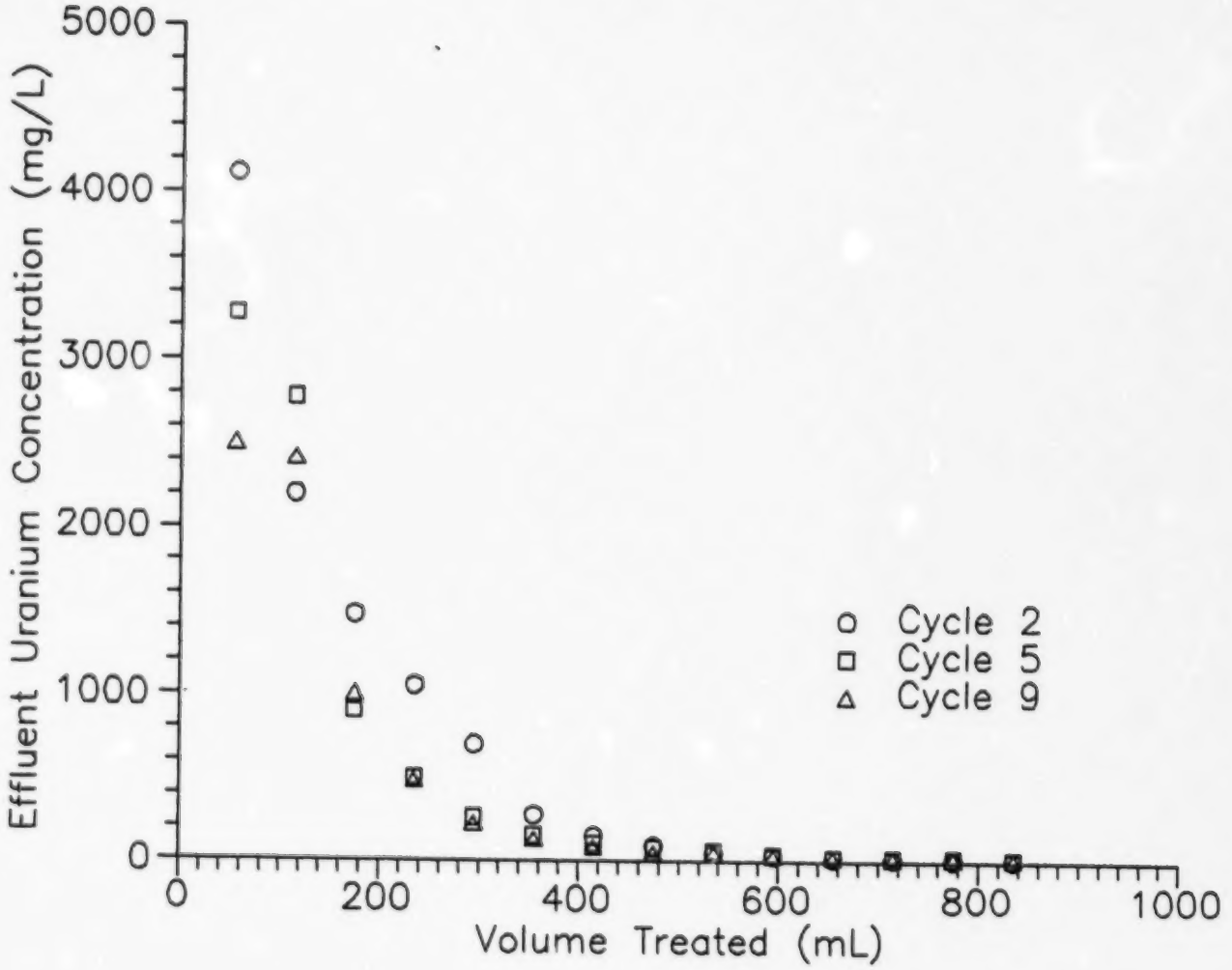

Figure 3.35 Elution Breakthrough Curves (Cycles 2, 5, and 9)

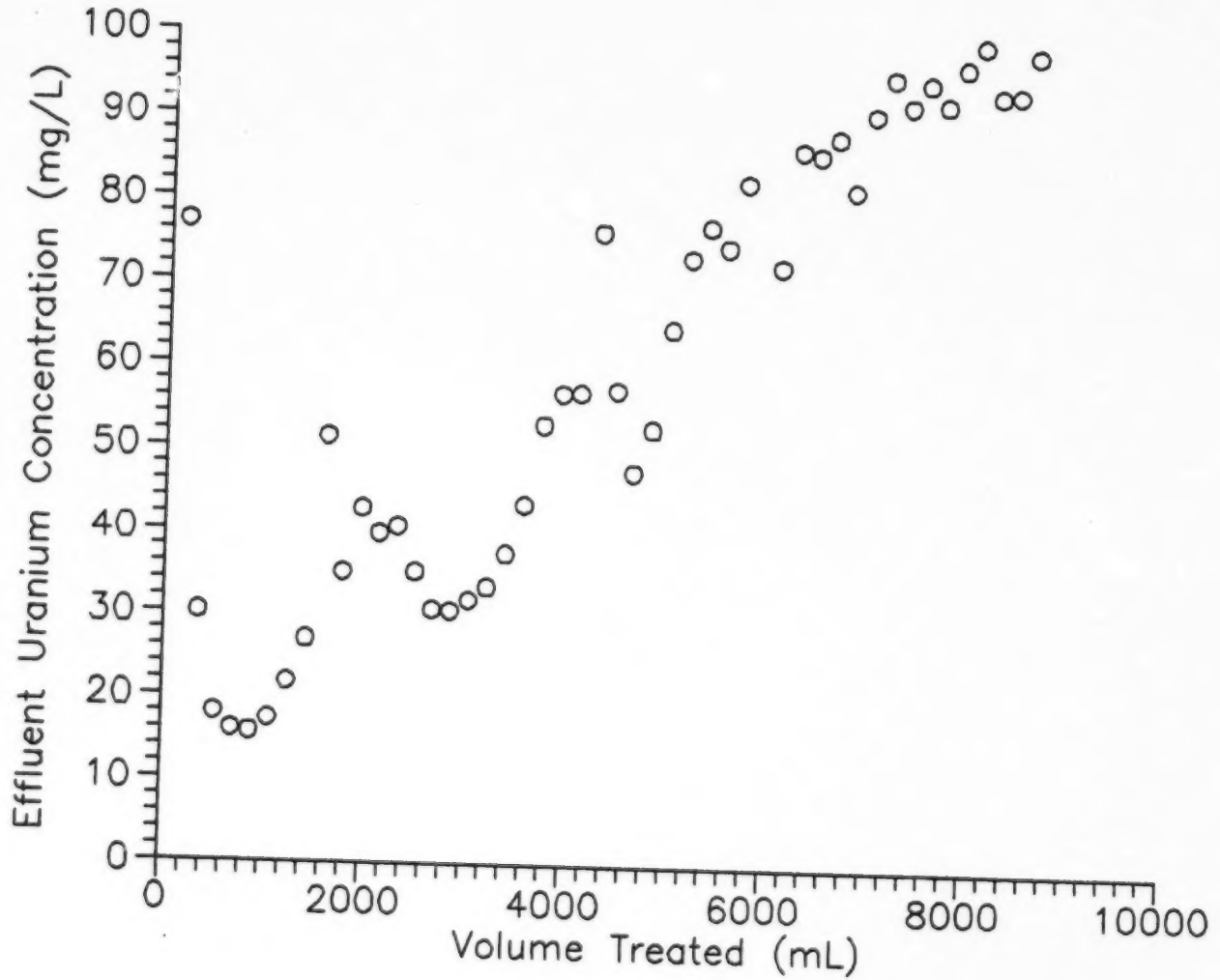

Figure 3.36 Loading Breakthrough Curve (Cycle 11) (Flow Rate = 3 mL/min)

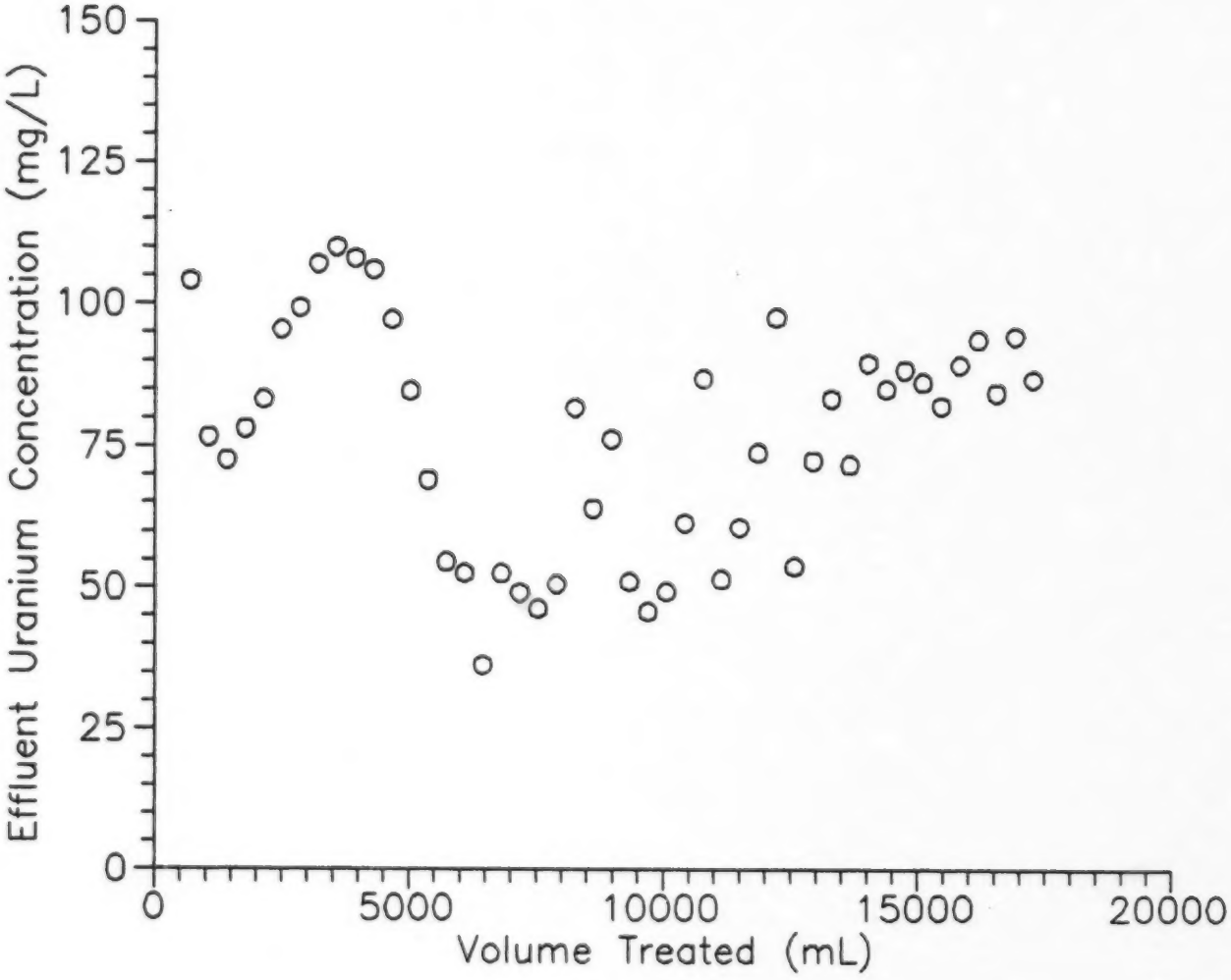

Figure 3.37 Loading Breakthrough Curve (Cycle 12) (Flow Rate = 6 mL/min)

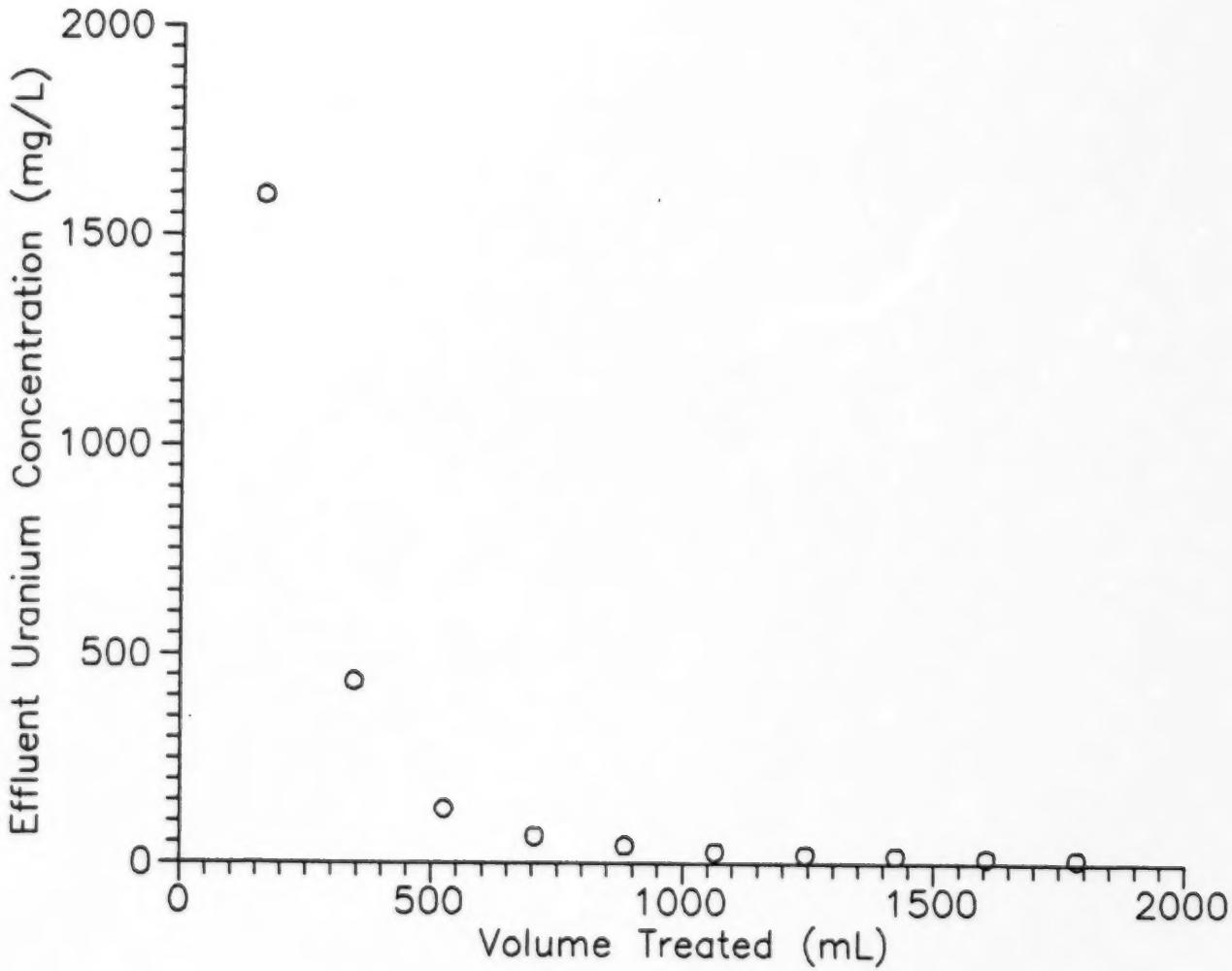

Figure 3.38 Elution Breakthrough Curve (Cycle 11) (Flow Rate = 3 mL/min)

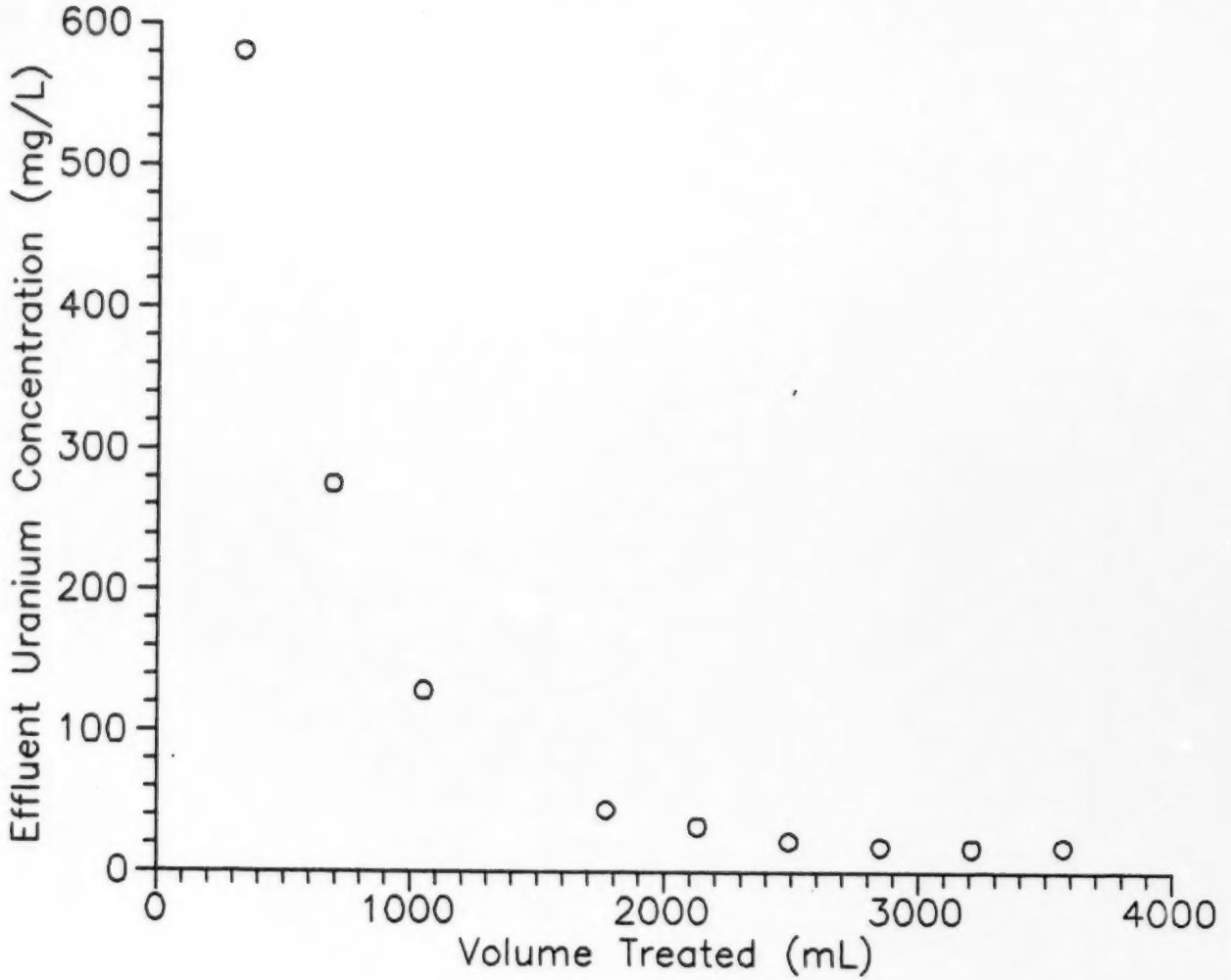

Figure 3.39 Elution Breakthrough Curve (Cycle 12) (Flow Rate = 6 mL/min)

4. CONCLUSIONS

The objectives outlined in section 1.1 of the present report have all been met successfully. Phase I of the present work has demonstrated that the immobilized biomass of R. arrhizus can be used in a batch mode, in at least 10 multiple cycles to quantitatively recover uranium from the bioleach solutions of Elliott Lake type ore. The biomass uranium uptake capacity appears to diminish as the cycles proceed.

The continuous laboratory scale pilot plant testing of the immobilized biomass of R. arrhizus for the recovery of uranium from the bioleach solutions of Elliot Lake type ore has suggested the following conclusions:

1. The behaviour of the immobilized biomass in the packed bed column was different than in the batch experiments as the reduction of the observed immobilized biomass uranium uptake capacity was smaller and stabilized faster (by the third cycle).
2. The immobilized biomass can be used effectively for at least 12 cycles with consistent performance.
3. The uranium uptake capacity of the immobilized biomass suffers an initial reduction of its uptake capacity and subsequently remains stable at about 50 mg/g.
4. The uranium uptake capacity of the immobilized biomass does not appear to be sensitive to the bioleach solution uranium concentration suggesting a flat equilibrium relationship with an uptake capacity of about 50 mg/g.
5. All the uranium that is retained by the immobilized biomass particles can be recovered during elution.
6. Eluate uranium concentrations of over 5000 mg/L are possible and further optimization of elution is possible.
7. The bioleach solution over-flow rate in the packed bed column did not affect the observed immobilized biomass uranium loading. It must be emphasized, however, that the adsorption zone was wider than the actual bed depth.

The conclusions from the second phase of the present work are very encouraging and suggest that a realistic potential exists for the industrial application of biosorption for uranium recovery from the bioleach solutions of Elliot Lake type ore using our immobilized biomass adsorbent. Further work, using a large size column is necessary (i) in order to examine the behaviour of the breakthrough curve in a deeper packed bed (ii) in order to confirm the biomass performance well beyond the 14 cycles and (iii) in order to optimize the elution conditions.

The investigation of the phenomena responsible for the observed change in the biomass uranium uptake capacity should also be pursued in order to maximize the efficiency of the biomass use in uranium recovery.

APPENDIX I

Results of Continuous Experiments

TABLE A1: Loading Breakthrough Data

Volume Treated (mg/L)	Effluent Uranium Concentration (mg/L) Cycle 1	2	3	4	5
55	3.5	116.0	139.0	228.0	173.0
115		28.7	72.4	48.4	73.9
175		16.0	42.2	87.2	44.7
235	0.7	14.5	25.0	28.2	32.6
295		8.9	20.7	22.8	27.2
355	1.1	5.7	18.2	21.2	23.9
415	1.5	6.6	20.5	19.1	27.2
475	4.2	9.8	24.6	23.6	29.3
535	6.3	8.5	31.3	23.6	32.8
595	9.2	14.7	31.0	25.3	38.3
655	10.2	14.5	33.6	26.0	47.7
715	12.4	16.8	29.4	27.8	33.7
775		20.8	38.7	34.8	14.4
835		18.9	51.5	32.2	106.0
895		28.7	60.3	32.0	33.8
955		49.3	74.4	62.3	83.8
1015		53.6	85.9	68.3	83.5
1075	32.2	66.6	106.0	97.1	99.1
1135	36.5	80.4	121.0	97.0	21.4
1195	39.4	88.2	129.0	107.0	111.0
1255	46.3	103.0	161.0	120.0	119.0
1315	53.2	107.0	157.0	123.0	136.0
1375	52.4	120.0	174.0	137.0	145.0
1435	59.5	125.0	171.0	142.0	146.0
1495		126.0	148.0	139.5	118.0
1555		136.0	155.0	139.0	132.0
1615		159.0	155.0	149.0	146.0
1675		153.0	170.0	161.0	158.0
1735		158.0	192.0	181.0	177.0
1795		168.0	207.5	183.0	173.0
1855		176.0	204.0	183.0	188.0
1915		186.0	214.0	196.0	204.0
1975		182.0	231.0	211.0	203.0
2035		176.0	232.0	207.0	205.0
2095		190.0	232.0	212.0	208.0
2155		213.0	234.0	217.0	198.0
2215		240.0	250.0	221.0	207.0
2275		228.0	222.0	220.0	212.0
2335		244.0	261.0	246.0	212.0
2395		293.0	245.0	240.0	224.0
2455		256.0	249.0	246.0	226.0
2515		257.0	253.0	246.0	238.0
2575		295.0	249.0	259.0	247.0
2635		257.0	262.0	253.0	258.0
2695		277.0	252.0	260.0	256.0
2755		292.0	269.0	258.0	259.0
2815		265.0	287.0	269.0	265.0
2875		265.0	279.0	267.0	268.0

TABLE A2: Loading Breakthrough Data

Volume Treated (mg/L)	Effluent Uranium Concentration Cycle 6	7	8	9
55	202.0	197.0	149.0	173.0
115	69.6	90.3	78.8	69.0
175	48.4	50.9	45.7	46.0
235	29.0	34.8	32.8	33.0
295	23.7	24.6	25.4	22.5
355	18.2	20.9	22.1	19.0
415	15.9	19.4	17.6	17.0
475	15.6	17.0	15.2	18.0
535	17.1	21.1	17.7	18.0
595	17.8	21.2	19.7	20.0
655	19.6	29.0	22.1	23.0
715	23.8	23.5	22.8	27.0
775	26.8	22.5	22.9	34.0
835	14.4	29.0	26.9	32.0
895	10.9	22.2	24.1	35.5
955	36.5	63.6	8.8	16.0
1015	41.5	62.3	12.7	10.0
1075	60.8	42.0	36.3	19.0
1135	81.9	85.2	64.3	66.0
1195	97.3	102.0	87.5	96.0
1255	117.0	116.0	110.0	116.0
1315	111.0	127.0	128.0	132.0
1375	139.0	141.0	142.0	138.0
1435	149.0	146.0	152.0	147.0
1495	136.0	122.0	109.0	87.5
1555	151.0	151.0	153.0	151.0
1615	161.0	166.0	0.0	153.0
1675	174.0	179.0	176.0	159.0
1735	184.0	190.0	196.0	174.0
1795	190.0	201.0	206.0	195.0
1855	200.0	209.0	0.0	207.0
1915	212.0	215.0	213.0	207.0
1975	216.0	209.0	219.0	206.0
2035	221.0	224.0	228.0	203.0
2095	219.0	229.0	231.0	204.0
2155	217.0	235.0	232.0	223.0
2215	226.5	227.0	229.0	215.0
2275	223.0	244.0	234.0	228.0
2335	233.0	243.0	236.0	226.0
2395	238.0	246.5	247.0	230.0
2455	247.0	240.0	241.0	220.0
2515	244.0	237.0	250.0	234.0
2575	245.0	264.0	247.0	219.0
2635	257.0	260.0	260.0	242.0
2695	264.0	269.0	257.0	243.0
2755	273.0	260.0	254.0	240.0
2815	266.0	266.0	252.0	251.0
2875	286.0	272.0	271.0	249.0

TABLE A3: Elution Breakthrough Data

Volume Treated (mg/L)	Effluent Uranium Concentration Cycle 1	2	3	4
55	5080.0	4115.0	5090.0	3590.0
115	2860.0	2200.0	2340.0	2570.0
175	1430.0	1480.0	1230.0	1180.0
235	857.0	1055.0	623.0	619.0
295	434.0	701.0	304.0	335.0
355	161.0	280.0	188.0	201.5
415	96.4	149.0	103.5	114.0
475	62.4	92.5	76.0	77.2
535	35.4	51.0	58.6	47.1
595	30.8	33.6	39.6	37.2
655	22.6	22.5	33.7	27.2
715	18.2	17.7	24.4	23.2
775	13.4	12.9	17.9	18.5
835	9.4	11.6	21.7	17.9

TABLE A4: Elution Breakthrough Data

Volume Treated (mg/L)	Effluent Uranium Concentration (mg/L) Cycle 6	7	8	9	10
55	3220.0	2315.0	1950.0	2500.0	1720.0
115	2205.0	2310.0	2475.0	2410.0	1820.0
175	910.0	978.0	1030.0	1007.0	915.0
235	504.0	494.0	518.0	486.0	435.0
295	243.0	233.0	237.0	228.0	196.0
355	121.0	121.0	131.0	134.0	109.0
415	84.7	78.8	86.9	84.5	61.6
475	58.8	56.7	67.3	52.6	65.0
535	46.1	38.5	50.6	49.6	48.5
595	34.4	34.0	40.8	37.1	42.6
655	29.8	27.5	31.3	27.9	44.8
715	23.7	23.8	27.1	22.9	34.8
775	19.8	21.4	21.5	23.6	29.5
835	19.4	16.8	19.3	20.9	21.4

TABLE A5: Breakthrough Data (Cycle 11)

Volume Treated (mg/L)	Effluent Uranium Concentration (mg/L)	
	Loading	Elution
165	77.0	1595.0
345	30.2	437.0
525	18.1	131.0
705	16.1	65.5
885	15.8	42.9
1065	17.4	29.0
1245	21.9	22.2
1425	27.0	19.3
1605	51.3	15.2
1785	35.1	12.5
1965	42.7	
2145	39.8	
2325	40.6	
2505	35.2	
2685	30.7	
2865	30.6	
3045	31.9	
3225	33.5	
3405	37.5	
3585	43.4	
3765	53.0	
3945	56.8	
4125	56.9	
4305	76.2	
4485	57.3	
4665	47.5	
4845	52.7	
5025	64.7	
5205	73.3	
5385	77.1	
5565	74.7	
5745	82.5	
6105	72.5	
6285	86.5	
6465	86.0	
6645	88.1	
6825	81.8	
7005	91.0	
7185	95.5	
7365	92.2	
7545	94.9	
7725	92.4	
7905	96.9	
8085	99.6	
8265	93.6	
8445	93.8	
8625	98.6	

TABLE A.6: Breakthrough Data (Cycle 12)

Volume Treated (mg/L)	Effluent Uranium Concentration (mg/L)	
	Loading	Elution
330	221.0	581.0
690	104.0	275.0
1050	76.5	129.0
1410	72.5	44.3
1770	78.0	32.7
2130	83.1	22.1
2490	95.4	18.6
2850	99.2	17.7
3210	107.0	18.4
3570	110.0	
3930	108.0	
4290	106.0	
4650	97.1	
5010	84.6	
5370	69.0	
5730	54.5	
6090	52.6	
6450	36.4	
6810	52.5	
7170	49.2	
7530	46.3	
7890	50.6	
8250	81.7	
8610	64.0	
8970	76.2	
9330	51.1	
9690	45.8	
10050	49.3	
10410	61.4	
10770	86.9	
11130	51.5	
11490	60.7	
11850	73.8	
12210	97.6	
12570	53.8	
12930	72.5	
13290	83.5	
13650	71.8	
14010	89.7	
14370	85.1	
14730	88.5	
15090	86.3	
15450	82.2	
15810	89.4	
16170	93.8	
16530	84.5	
16890	94.5	
17250	86.9	

TABLE A.7: Loading Cycle Process Data

Cycle	Uranium Concentration (mg/L) Effluent	Column Drainage	Rinse
1	65.6	204	41.8
2	115	240	47.2
3	121	245	54.0
4	132	230	49.3
5	138	236	59.2
6	131	246	56.1
7	144	257	61.2
8	129	233	59.8
9	128	234	57.8
10	216	296	77.2
11	63.7	104	30.7
12	94.3	106	32.6

TABLE A.8: Elution Cycle Process Data

Cycle	Uranium Concentration (mg/L) Effluent	Column Drainage	Rinse
1	679	3.9	1.2
2	513	5.9	2.3
3	445	4.0	3.6
4	428	6.2	2.4
5	430	6.4	2.1
6	412	6.7	2.1
7	407	17.7	3.5
8	426	5.8	2.2
9	379	7.6	2.5
10	272	6.2	2.0
11	218	14.1	6.4
12	95.0	11.0	5.9